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Computer modeling of photochemical ozone formation: a simplified approach

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COMPUTER MODELING OF PHOTOCHEMICAL OZONE FORMATION: A SIMPLIFIED APPROACH

by

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Photochemically produced ozone represents a worldwide environmental hazard. Controlling ozone formation in polluted air requires control of hydrocarbon and nitrogen oxides precursors. The degree of control can be established

with the chemical model of the reacting species. A hydrocarbon-specific photochemical ozone model is developed, based upon a minimum set of chemical equations. This model eliminates the need for the traditional "brute force" approach to integrate systems of tens or even hundreds of simultaneous differential equations. We have sought to develop the full kinetic potential for simplification which this chemical system may have. Key features of the model are reaction of parent hydrocarbon with hydroxyl radical (OH) to produce products, which themselves react with OH or are photodissociated. These basic steps are summarized by three rate parameters which describe NO photooxidation and ultimate accumulation of ozone. Since the mechanism may be solved in a closed form, it is a simple matter to evaluate the rate parameters for any hydrocarbon from smog chamber data. This evaluation can be carried out by analysis of data in NO photooxidation regime, before ozone begins to accumulate. The simple model for NO photooxidation is transformed to give an equation which describes the number of NO conversions per hydrocarbon decay, independent of time or of hydroxyl radical concentration. Comparison of the rate parameters determined from existing smog chamber data for n-butane and propene shows a very good agreement with explicit mechanisms for these extensively studied hydrocarbons. Rate parameters have been determined for a number of less studied hydrocarbons as well.

DEDICATION

This work is dedicated to my adorable wife, Soraya, for her gift of perseverance and love; and to my two lovely daughters Roya and Jina.

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CHAPTER I

INTRODUCTION

I-a History

As initiated by the energy of the sun, the series of atmospheric photochemical reactions between hydrocarbons (HC) and oxides of nitrogen (NOx=NO+NO2), which leads to the formation of new products, is a very complex system (1-4). Among the various products of the HC-NOx system, collectively called "smog", there are substances termed photochemical oxidants. The term "photochemical oxidant" is used by convention to define those atmospheric pollutants that are capable of oxidizing iodide ions in a neutral-buffered solution (5).

The problems associated with photochemical oxidants have been known to exist in the United States for more than 40 years. The first manifestation of the problem occurred the Los Angeles area and included accelerated deterioration of rubber products, damage to vegetation, and eye irritation (6-8). While the problem is severest in the southwest part of the U.S, high levels of oxidants are known to occur in

every major urban center in this country and, through short and long range transport, oxidant spreads to non-urban areas and even to other countries (9).

Extensive research has uneqivocally identified several components of photochemical oxidant mixtures (7,10-11). Thus, photochemical oxidants are known to consist mainly of ozone (O3), nitrogen dioxide (NO2), peroxyacetyl nitrate (PAN) and in lesser amounts, other peroxy acyl nitrates (RCO3NO2), hydroperoxide (HO2) and alkylperoxides (RO2). Among various photochemical smog constituents, ozone has received the most attention and has been singled out and treated as the sole representative of the chemical system and has been given most of the research attention. This should not be interpreted to suggest that other photochemical pollutants are thought to be of less concern. Rather, it reflects the fact that the ozone pollution problem is more easily measured and, hence, more amenable to research than eye irritation, plant damage, and visibility reduction problems associated with other pollutants, and the assumption that the abatement of ozone will in all probability alleviate the other photochemical pollution problems also. The other reason that ozone has received much attention is its high toxicity. Several correlative observations have suggested adverse effects of ozone upon plants, human and animal health (12-15). The cost of photochemical smog, in terms of economic losses and

detriment to human and non-human ecology, is enormous (16).

After the pioneering work of Haggen-Smit in 1952 which lead to the characterization of the nature of photochemical oxidants (10), considerable research has been devoted toward elucidating the mechanism by which ozone is formed in the atmosphere. In 1961, Leighton published an accurate and reasonably complete description of the photochemistry of air pollution (1). Since that time additional information on chemical kinetics and mechanistic studies of elementary reactions thought to be significant in the formation of photochemical smog have served to further improve our general understanding of the process (11,17-22). By late 1960 and early 1970 the picture had become sufficiently complete that formulation of kinetic mechanisms for mathematical simulation of photochemical smog formation was possible. These mechanisms were based upon data obtained in controlled simulated atmospheres. Although different approaches (discribed in chapter II) have been used to model the mechanism by which photochemical smog is formed in the atmosphere, most of the existing modelling attempts are suffering from several deficiencies. Before introducing the different modelling approaches, the remainder of this chapter will provide some general background material. Section I-b discusses the various natural and anthropogenic sources of ozone in the atmosphere. Section I-c describes the general mechanism by which ozone is formed

through the NOx-photolytic cycle. Chapter II is devoted to comparison between existing modelling attempts and our approach. The basic assumptions and approximations required for our model are described in chapter III. Chapter IV developes the required equations for our model and the capabilities of this model are illustrated. Chapter V contains information on smog chamber experiments. Chapter VI describes validation of the model over a wide range of HC/NOx ratios. Conclusion, recommendations and expected benefits of this research are included in chapter VII.

I-b Sources of Ozone

Ozone found in the lower level of the earth's atmosphere (troposphere) has been traced to both natural and anthropogenic sources. Research on natural ozone identified a number of sources, of which stratospheric ozone intrusion, electric discharge, and photooxidation of naturally occurring organic matter appeared to have the highest contributions (23-26). Although the magnitude of each natural source is not exactly known, it has been suggested that the contribution of the natural ozone concentration should not be overlooked in control strategy planning (27). The observed 30-50 ppb background ozone concentration is attributed mainly to the photooxidation of the naturally occurring hydrocarbons such as methane and more reactive but less abundant non-methane hydrocarbons in the presence of oxides of nitrogen (28-30). Formation of ozone is accomplished through a series of catalytic reactions with the highly reactive hydroxyl (OH) and hydroperoxy (HO2) radicals. The photochemical source of tropospheric ozone was postulated to account for the hemispheric assymetry in the tropospheric ozone distribution which was derived from ozonesonde ballon data by Fishman and Crutzen (24,31-32).

Ozone from anthropogenic sources is a product of atmospheric photochemical reactions involving primary pollutants (HC,NOx) and atmospheric oxygen. Use of coal and

petroleum products such as natural gas, gasoline, and fuel oil, all termed "fossil fuel", is responsible for most of the air pollution in urban atmospheres. The remainder comes from solvent evaporation. Fossil fuels are composed principally of hydrocarbons which, upon complete combustion, produce two oxides, carbon dioxide (CO2) and water (H2O). These two oxides are not considered to be air pollutants, since they are relatively non-toxic and are normal constituents of the atmosphere. The byproducts of combustion in exhaust gases and the products of incomplete combustion lead to localized air pollution. Since combustion processes are usually less than 100 percent efficient, the exhaust gases contain minor amounts of the original fuel as well as minor amounts of partially oxidized fuel such as carbon monoxide (CO) and aldehydes (33). Also a small amount of nitrogen, a major constituent of air, is oxidized at high temperatures characteristic of combustion process occuring in internal combustion engines, incinerators, power plants etc. The high temperature characteristic of combustion process provides a driving force for the following reaction which otherwise is not spontaneous

$$N2 + O2 \text{ -----> } 2NO$$

Nitric oxide is colourless and relatively non-toxic, and since it does not absorb in the component of sunlight which

reaches the earth's surface (wavelenght 300-700 nm) it cannot initiate the photooxidation sequence. Unfortunately nitric oxide can be converted to nitogen dioxide in a thermal reaction with oxygen

$$2NO + O_2 \longrightarrow 2NO_2$$

Since this reaction is third-order, it is important only during the early stages of dilution of the exhaust gases, when nitric oxide is in high local concentration. Once atmospheric dilution has reduced the concentration of nitric oxide to the ppm range, thermal oxidation is too slow to oxidize a significant amount of nitric oxide. However, there are other important reactions in polluted atmospheres which bring about the conversion. Detailed understanding of this conversion is vital for an accurate formulation of a kinetic mechanism. Once NO2 is formed, it will initiate a series of reactions leading to the formation of ozone and other photochemical smog components. This conversion is discussed in the following section.

I-c NOX-Photolytic Cycle

Ozone is the most abundant photochemical oxidant found in the troposphere. In order to photochemically generate these observed O3 concentrations, a process other than direct absorption by O2 must be involved. Light absorption by O2 does not occur in the troposphere, since the short ultraviolet wavelenghts (240 nm) responsible for this reaction do not reach the earth's lower atmosphere. Furthermore, only a small portion of the ozone observed in polluted air could have been transported from the stratosphere, where high concentration exist naturally (27). Consequently other generation process must be involved. Among various atmospheric pollutants, nitrogen dioxide (NO2) is the most efficient absorber of that portion of the sun's ultraviolet light which reaches the earth's surface. Absorption of light with wavelenght of less than 430 nm results in the photodissociation (34)

$$NO2 + h\nu \longrightarrow NO + O \qquad (1)$$

This important process, producing highly reactive oxygen atoms in their ground electronic state, is the source of tropospheric ozone formed by equation 2:

$$O + O2 + M \longrightarrow O3 + M \qquad (2)$$

$$O3 + NO \longrightarrow NO2 + O2 \qquad (3)$$

These reactions may be explained as follows. In reaction 1, the energy contained in the ultraviolet light (hv) acting upon the NO2 molecules is sufficient to break its bond, yielding NO and O. The most probable fate of the atomic oxygen thus formed is reaction with molecular oxygen in the atmosphere to form ozone. Reaction 2 actually proceeds in two steps. An atomic oxygen reacts with O2 to form energy-rich O3 molecule. In the absence of a means to remove this excess energy, the O3 decomposes rapidly back to O2 and an O atom. Collision with another molecule in the air, however, will result in the transfer of the some of its excess energy, leading to formation of the stable O3 molecule. This collisional molecule is indicated by the symbol M in reaction 2. It can be any molecule in the system. In air, the collision will probably occur with N2 or O2, since these account for most of the molecules present. Reaction 3 shows that O3 reacts with NO to reform the original molecule (NO2) and complete the cycle. Reations 1-3 establish a steady state concentration of products and reactants:

$$NO2 + O2 \underset{k_2}{\overset{k_1[h\nu]}{\rightleftharpoons}} NO + O3 \qquad (4)$$

For a detailed discussion of this photo-induced equilibrium see Leighton (1) and Stephens (35).

Under steady-state condition the concentration of ozone is

$$[O3]_{P.S.} = (k1[NO2]) / (k3[NO]) \quad \text{or} \quad O3_{P.S.} = O3\ (NOx) \qquad (5)$$

where $[O3]_{P.S.}$ is the photostationary concentration of ozone and its magnitude depends upon the initial proportions of NO + NO2 and the light intensity.

In the presence of hydrocarbons, this dynamic equilibrium is perturbed. This can be seen in the plot of species concentration vs. irradiation time for the propene-NOx system in Fig (1). As time progress, nitric oxide is oxidized almost completely to nitrogen dioxide. Ozone which was initially present at steady-state concentration, now builds up with the disappearance of nitric oxide. This disappearance of nitric oxide and the consequent build up of NO2 strongly suggest that the presence of hydrocarbon converts nitric oxide to nitrogen dioxide. This conversion can be explained by the following equations:

HC + OX -----> RO2 (6)

RO2+ NO -----> NO2 (7)

Hydrocarbon degradation by oxidizing agents (OX), e.g. OH and O3, results in the formation of intermediates (RO2) which are capable of converting NO --> NO2. Therefore, in the presence of hydrocarbons, peroxyradicals are formed which compete with ozone for removal of nitric oxide. As a consequence less ozone will be depleted through its reaction with nitric oxide, reaction (3), and this provides a path by which ozone accumulates. The ozone concentration under this

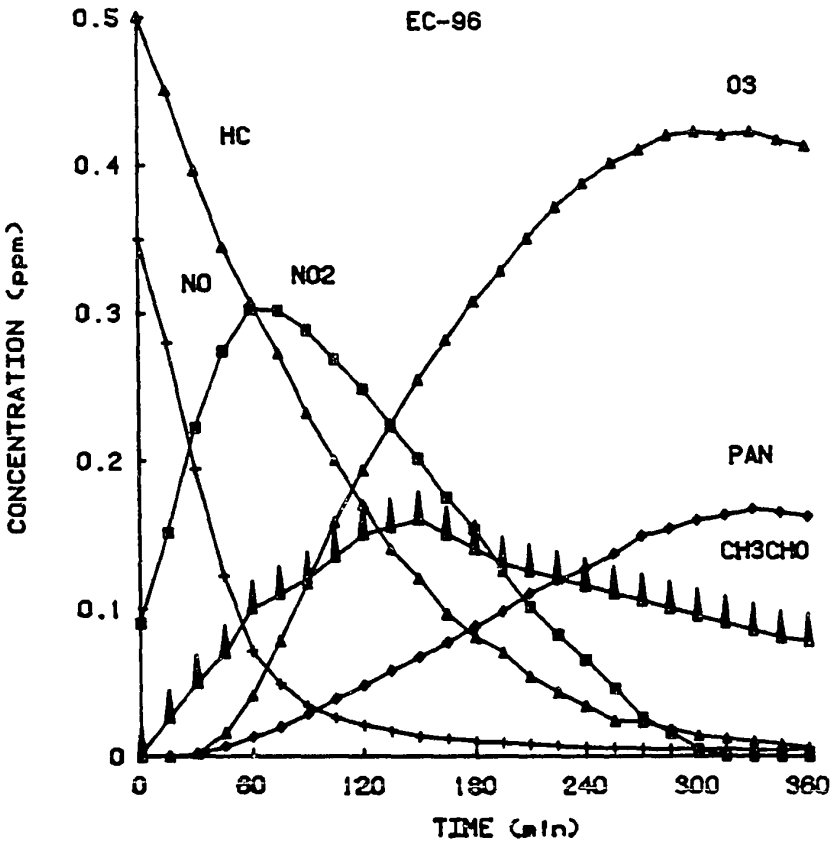


Figure 1. Concentration vs. irradiation time for propene/NO_x.

circumstance would be

$$[O3] = [O3]_{P.S.} + [O3]_{Perturb} \quad \text{or} \quad O3=O3(NOx,HC) \qquad (8)$$

Here $[O3]_{Perturb}$ is the concentration of ozone due to perturbation of the NOx photolytic cycle by hydrocarbons.

I-d Key elements of smog system for development of the simplified model

In order to estimate the concentration of ozone in this circumstance, three major parameters are required: hydrocarbon abundance, hydrocarbon reactivity, and the ability of the hydrocarbon to oxidize NO to NO2. Reactivity is adopted as the elementary rate constant for attack of OH on each hydrocarbon (36). Although extensive information on the rate constants of various hydrocarbons with OH is available (37), very little is known about the stoichiometry of the conversion of NO to NO2 for various hydrocarbons of atmospheric importance. Once that information becomes available, one can accurately predict the rate of the ozone formation and from that the ozone maximum could be calculated. Knowledge of the stoichiometry coefficients for nitric oxide photooxidation can also be used to refine the current concept of reactivity (36), since two hydrocarbons might have similar value for the rate constant for the reaction with hydroxyl radical, but not necessarily identical efficiency for converting NO to NO2. In addition, for an accurate assessment of the hydrocarbon reactivity, the contribution of the products of the hydrocarbon must also be considered. Since the reactivity of a given hydrocarbon toward nitric oxide photooxidation and ozone formation obviously is a function of the products

it forms, ignoring those processes in the model of a parent hydrocarbons's reactivity is a major oversight. Our mathematical model incorporates the above facts explicitly.

CHAPTER II

CHEMICAL MODELS FOR PHOTOCHEMICAL OZONE FORMATION

The current Federal Ozone Standard of 0.12 ppm is routinely exceeded in many areas of the United States and extremely expensive hydrocarbon and nitrogen oxide control strategies are currently in effect or contemplated to combat this problem. Considerable effort has been expended historically to develop chemical models which accurately describe the relationship of photochemically produced ozone to precursor hydrocarbon and NOx concentrations. Without such a model cost effective ozone control strategies are very difficult (38). Chemical models are generally of two types. The first is an explicit or detailed model which attempts to deal accurately with each chemical reaction step occuring. Typically such a model incorporates 20-40 inorganic reactions and between 50-110 organic specific reactions. Such models have been developed to a very detailed extent for n-Butane/NOx and Propene/NOx and for a limited number of other hydrocarbos as well (39-43). An example of a detailed mechanism for the Propene/NOx system is presented in table (I). In this modelling approach it is

TABLE I

EXPLICIT MECHANISM FOR PROPENE/NO_x (41)

reaction no.	reaction	rate constant[a]
	Photochemical Reactions[b]	
1	$NO_2 + h\nu \rightarrow NO + O(^3P)$	1.0
2	$O_3 + h\nu \rightarrow O(^1D) + O_2$	3.9×10^{-3}
3	$\rightarrow O(^3P) + O_2$	2.0×10^{-5}
4	$HONO + h\nu \rightarrow OH + NO$	1.5×10^{-1}
5	$H_2O_2 + h\nu \rightarrow 2OH$	4.9×10^{-6}
6	$NO_3 + h\nu \rightarrow NO + O_2$	4.3
7	$\rightarrow NO_2 + O(^3P)$	1.3×10^{1}
8	$HCHO + h\nu \rightarrow H + HCO$	2.0×10^{-5}
9	$\rightarrow H_2 + CO$	6.3×10^{-5}
10	$CH_3CHO + h\nu \rightarrow CH_3 + HCO$	2.6×10^{-6}
11	$C_2H_5CHO + h\nu \rightarrow C_2H_5 + HCO$	2.6×10^{-6}
12	$CH_3COCHO + h\nu \xrightarrow{O_2} CH_3C(O)O_2 + HCO$	1.5×10^{-1}
13	$CH_3COCH_2OH + h\nu \xrightarrow{O_2} CH_3C(O)O_2 + CH_2OH$	9.0×10^{-4}
14	$CH_3CH(OH)CHO + h\nu \rightarrow CH_3CHOH + HCO$	2.6×10^{-5}
15	$CH_3CO + h\nu \xrightarrow{O_2} CH_3O_2 + CO$	2.4×10^{-5}
16	$\xrightarrow{O_2} CH_2OO + CO$	9.7×10^{-4}
17	$CH_3ONO + h\nu \rightarrow CH_3O + NO$	1.3×10^{-1}
18	$C_2H_5ONO + h\nu \rightarrow C_2H_5O + NO$	1.3×10^{-1}
	Inorganic Reactions	
19	$O(^3P) + O_2 + M \rightarrow O_3 + M$	3.6×10^{-32}
20	$O(^3P) + NO \rightarrow NO + O_2$	9.1×10^{-12}
21	$O(^3P) + NO_2 + M \rightarrow NO_3 + M$	1.0×10^{-31}
22	$O(^3P) + NO + M \rightarrow NO_2 + M$	1.1×10^{-31}
23	$O(^3P) + O_2 \rightarrow 2O_2$	9.6×10^{-11}
24	$O(^1D) + M \rightarrow O(^3P) + M$	2.8×10^{-11}
25	$O(^1D) + H_2O \rightarrow 2OH$	2.3×10^{-10}
26	$O(^1D) + O_2 \rightarrow 2O_2$	2.4×10^{-11}
27	$O_3 + NO \rightarrow NO_2 + O_2$	1.8×10^{-14}
28	$O_3 + NO_2 \rightarrow NO_3 + O_2$	3.7×10^{-17}
29	$O_3 + OH \rightarrow HO_2 + O_2$	5.5×10^{-14}
30	$O_3 + HO_2 \rightarrow OH + 2O_2$	1.1×10^{-14}
31	$2NO + O_2 \rightarrow 2NO_2$	1.9×10^{-38}
32	$NO + NO_3 \rightarrow 2NO_2$	1.9×10^{-11}
33	$NO + OH \rightarrow HONO$	1.2×10^{-11}
34	$NO + HO_2 \rightarrow OH + NO_2$	8.1×10^{-12}
35	$NO_2 + NO_3 \rightarrow N_2O_5$	1.9×10^{-12}
36	$N_2O_5 \rightarrow NO_2 + NO_3$	3.7×10^{-1}
37	$NO_2 + OH \rightarrow HNO_3$	1.2×10^{-11}
38	$NO_2 + HO_2 \rightarrow HO_2NO_2$	1.3×10^{-1}
39	$HO_2NO_2 \rightarrow HO_2 + NO_2$	2.5×10^{-12}
40	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.5×10^{-12}
41	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	8.4×10^{-12}
42	$CO + OH \rightarrow H + CO_2$	3.0×10^{-13}
43	$H + O_2 + M \rightarrow HO_2 + M$	1.7×10^{-32}
	Wall Loss Reactions	
44	$O_3 \rightarrow O_2$ (wall)	1.1×10^{-4}, 1.6×10^{-6}
45	$NO_2 \rightarrow NO_2$ (wall)	7.2×10^{-4}, 1.1×10^{-6}
	Propene + $O(^3P)$ Reaction System	
46	$C_3H_6 + O(^3P) \rightarrow C_2H_5 + HCO$	2.3×10^{-12}
47	$\rightarrow CH_3CHCH_2O$	1.1×10^{-12}
48	$\rightarrow C_2H_5CHO$	1.1×10^{-12}
49	$HCO + O_2 \rightarrow HO_2 + CO$	5.6×10^{-12}
50	$CH_3 + O_2 \rightarrow CH_3O_2$	fast
51	$C_2H_5 + O_2 \rightarrow C_2H_5O_2$	fast
52	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	8.0×10^{-12}
53	$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	8.0×10^{-12}
54	$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.3×10^{-11}
55	$CH_3O_2NO_2 \rightarrow CH_3O_2 + NO_2$	1.0×10^{1}
56	$C_2H_5O_2 + NO_2 \rightarrow C_2H_5O_2NO_2$	1.3×10^{-11}
57	$C_2H_5O_2NO_2 \rightarrow C_2H_5O_2 + NO_2$	1.0×10^{1}
58	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	2.9×10^{-12}
59	$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$	2.9×10^{-12}
60	$2CH_3O_2 \rightarrow 2CH_3O + O_2$	1.6×10^{-13}
61	$\rightarrow CH_3OH + HCHO + O_2$	2.7×10^{-13}
62	$\rightarrow CH_3OOCH_3$	3.0×10^{-14}
63	$2C_2H_5O_2 \rightarrow C_2H_5OOC_2H_5$	4.6×10^{-14}
64	$CH_3O + NO \rightarrow CH_3ONO$	1.7×10^{-11}
65	$\rightarrow HCHO + HNO$	3.0×10^{-12}
66	$C_2H_5O \rightarrow C_2H_5ONO$	1.7×10^{-11}
67	$\rightarrow CH_3CHO + HNO$	3.0×10^{-12}
68	$CH_3O + NO_2 \rightarrow CH_3ONO_2$	1.4×10^{-11}
69	$\rightarrow HCHO + HNO$	2.4×10^{-12}
70	$C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$	1.4×10^{-11}

TABLE I

(continued)

71	→ $CH_2CHO + HNO$	2.4×10^{-13}
72	$CH_2O + O_2 \rightarrow HCHO + HO_2$	6.8×10^{-12}
73	$C_2H_2O + O_2 \rightarrow CH_2CHO + HO_2$	6.8×10^{-16}
74	$CH_2C(O)O_2 + NO \rightarrow CH_3 + CO_2 + NO_2$	2.0×10^{-11}
75	$CH_2C(O)O_2 + NO_2 \rightarrow CH_2C(O)O_2NO_2$	1.3×10^{-11}
76	$CH_2C(O)O_2NO_2 \rightarrow CH_2C(O)O_2 + NO_2$	8.0×10^{-4}
77	$CH_2C(O)O_2 + HO_2 \rightarrow CH_2C(O)O_2H + O_2$	3.0×10^{-13}
78	$C_2H_2C(O)O_2 + NO \rightarrow C_2H_3 + CO_2 + NO_2$	2.0×10^{-11}
79	$C_2H_2C(O)O_2 + NO_2 \rightarrow C_2H_2C(O)O_2NO_2$	1.3×10^{-11}
80	$C_2H_2C(O)O_2NO_2 \rightarrow C_2H_2C(O)O_2 + NO_2$	8.0×10^{-4}
81	$C_2H_2C(O)O_2 + HO_2 \rightarrow C_2H_2C(O)O_2H + O_2$	3.0×10^{-13}
	Propene + O_3 Reaction System	
82	$C_3H_6 + O_3 \rightarrow CH_2CHO_2^{\ddagger} + HCHO$	5.5×10^{-15}
83	→ $CH_2CHO + CH_2O_2^{\ddagger}$	5.5×10^{-15}
84	$CH_2O_2^{\ddagger} \rightarrow$ [CH_2O_2]	(0.50)
85	→ CH_2OO	(0.50)
86	$CH_2CHO_2^{\ddagger} \rightarrow$ [CH_2CHO_2]	(0.50)
87	→ CH_2CHOO	(0.50)
88	$CH_2O_2 + NO \rightarrow HCHO + NO_2$	1.9×10^{-11}
89	$CH_2CHO_2 + NO \rightarrow CH_2CHO + NO_2$	1.9×10^{-11}
90	$CH_2O_2 + NO_2 \rightarrow HCHO + NO_3$	2.0×10^{-12}
91	$CH_2CHO_2 + NO_2 \rightarrow CH_2CHO + NO_3$	2.0×10^{-12}
92	$CH_2O_2 + HCHO \rightarrow$ product	1.4×10^{-15}
93	$CH_2O_2 + CH_2CHO \rightarrow$ product	1.4×10^{-15}
94	$CH_2CHO_2 + HCHO \rightarrow$ product	1.4×10^{-15}
95	$CH_2CHO_2 + CH_2CHO \rightarrow$ product	1.4×10^{-15}
96	[CH_2OO] → $H_2 + CO_2$	(0.18)
97	→ $CO + H_2O$	(0.67)
98	→ $2H + CO_2$	(0.09)
99	→ $HCHO$	(0.06)
100	[CH_2CHOO] → $CH_3 + CO_2$	(0.24)
101	→ $CH_3 + CO + OH$	(0.27)
102	→ $CH_2 + H + CO_2$	(0.35)
103	→ $CH_2O + H + CO$	(0.06)
104	→ $CH_2CO + H_2O$	(0.08)
	Propene + OH Reaction System	
105	$C_3H_6 + OH \xrightarrow{O_2} CH_2CH(O_2)CH_2OH$	1.8×10^{-11}
106	$C_3H_6 + OH \xrightarrow{O_2} CH_2CH(OH)CH_2O_2$	8.6×10^{-12}
107	$CH_2CH(O_2)CH_2OH + NO \rightarrow CH_2CH(O)CH_2OH$	1.9×10^{-11}
108	→ $CH_2CH(ONO_2)CH_2OH$	8.0×10^{-13}
109	$CH_2CH(OH)CH_2O_2 + NO \rightarrow CH_2CH(OH)CH_2O + NO_2$	1.9×10^{-11}
110	→ $CH_2CH(OH)CH_2ONO_2$	8.0×10^{-13}
111	$CH_2CH(O_2)CH_2OH + NO_2 \rightarrow CH_2CH(O_2NO_2)CH_2OH$	1.3×10^{-11}
112	$CH_2CH(O_2NO_2)CH_2OH \rightarrow CH_2CH(O_2)CH_2OH + NO_2$	1.0×10^{1}
113	$CH_2CH(OH)CH_2O_2 + NO_2 \rightarrow CH_2CH(OH)CH_2O_2NO_2$	1.3×10^{-11}
114	$CH_2CH(OH)CH_2O_2NO_2 \rightarrow CH_2CH(OH)CH_2O_2 + NO_2$	1.0×10^{1}
115	$CH_2CH(O)CH_2OH \rightarrow CH_2CHO + CH_2OH$	4.7×10^{4}
116	$CH_2C(OH)CH_2O \rightarrow CH_2CHOH + HCHO$	6.0×10^{5}
117	$CH_2OH + O_2 \rightarrow HCHO + HO_2$	fast
118	$CH_2CHOH + O_2 \rightarrow CH_2CHO + HO_2$	fast
119	$CH_2CH(O)CH_2OH + O_2 \rightarrow CH_2C(O)CH_2OH + HO_2$	1.2×10^{-12}
120	$CH_2CH(OH)CH_2O + O_2 \rightarrow CH_2CH(OH)CHO + HO_2$	1.2×10^{-12}
121	$CH_2CH(O_2)CH_2OH + HO_2 \rightarrow CH_2CH(O_2H)CH_2OH + O_2$	2.9×10^{-13}
122	$CH_2CH(OH)CH_2O_2 + HO_2 \rightarrow CH_2CH(OH)CH_2O_2H + O_2$	2.9×10^{-13}
123	$CH_2C(O)CH_2OH + OH \rightarrow CH_2C(O)CH(OH) + H_2O$	7.0×10^{-13}
124	$CH_2C(O)CHOH + O_2 \rightarrow CH_2C(O)CHO + HO_2$	fast
125	$CH_2CH(OH)CHO + OH \rightarrow CH_2C(OH)CHO + H_2O$	1.3×10^{-11}
126	$CH_2C(OH)CHO + O_2 \rightarrow CH_2C(O)CHO + HO_2$	fast
127	$CH_2CH(OH)CHO + OH \rightarrow CH_2CH(OH)CO + H_2O$	1.6×10^{-11}
128	$CH_2CH(OH)CO + O_2 \rightarrow CH_2CH(OH)C(O)O_2$	fast
129	$CH_2CH(OH)C(O)O_2 + NO \rightarrow CH_2CH(OH)CO_2 + NO_2$	2.0×10^{-11}
130	$CH_2CH(OH)CO_2 \rightarrow CH_2CHOH + CO_2$	fast
131	$CH_2CH(OH)C(O)O_2 + NO_2 \rightarrow CH_2CH(OH)C(O)O_2NO_2$	1.3×10^{-11}
132	$CH_2CH(OH)C(O)O_2NO_2 \rightarrow CH_2CH(OH)C(O)O_2 + NO_2$	8.0×10^{-4}
133	$CH_2C(O)CHO + OH \rightarrow CH_2C(O)CO + H_2O$	1.6×10^{-11}
134	$CH_2C(O)CO \rightarrow CH_2CO + CO$	fast
	Propene–NO_2 Reaction System	
135	$C_3H_6 + NO_2 \xrightarrow{O_2} CH_2CH(O_2)CH_2ONO_2$	5.5×10^{-13}
136	$\xrightarrow{O_2} CH_2CH(ONO_2)CH_2O_2$	2.7×10^{-13}
137	$CH_2CH(O_2)CH_2ONO_2 + NO \rightarrow CH_2CH(O)CH_2ONO_2 + NO_2$	1.9×10^{-11}
138	→ $CH_2CH(ONO_2)CH_2ONO_2$	8.0×10^{-13}
139	$CH_2CH(ONO_2)CH_2O_2 + NO \rightarrow CH_2CH(ONO_2)CH_2O + NO_2$	1.9×10^{-11}
140	→ $CH_2CH(ONO_2)CH_2ONO_2$	8.0×10^{-13}
141	$CH_2CH(O_2)CH_2ONO_2 + NO_2 \rightarrow CH_2CH(O_2NO_2)CH_2ONO_2$	1.3×10^{-11}
142	$CH_2CH(O_2NO_2)CH_2ONO_2 \rightarrow CH_2CH(O_2)CH_2ONO_2 + NO_2$	1.0×10^{1}
143	$CH_2CH(ONO_2)CH_2O_2 + NO_2 \rightarrow CH_2CH(ONO_2)CH_2O_2NO_2$	1.3×10^{-11}
144	$CH_2CH(ONO_2)CH_2O_2NO_2 \rightarrow CH_2CH(ONO_2)CH_2O_2 + NO_2$	1.0×10^{1}
145	$CH_2CH(O_2)CH_2ONO_2 + HO_2 \rightarrow CH_2CH(OOH)CH_2ONO_2 + O_2$	2.9×10^{-13}
146	$CH_2CH(ONO_2)CH_2O_2 + HO_2 \rightarrow CH_2CH(ONO_2)CH_2OOH + O_2$	2.9×10^{-13}
147	$CH_2CH(O)CH_2ONO_2 + NO_2 \rightarrow CH_2CH(ONO_2)CH_2ONO_2$	1.4×10^{-11}
148	$CH_2CH(ONO_2)CH_2O + NO_2 \rightarrow CH_2CH(ONO_2)CH_2ONO_2$	1.4×10^{-11}
149	$CH_2CH(O)CH_2ONO_2 + O_2 \rightarrow CH_2C(O)CH_2ONO_2 + HO_2$	3.0×10^{-15}
150	$CH_2CH(ONO_2)CH_2O + O_2 \rightarrow CH_2CH(ONO_2)CHCHO + HO_2$	3.0×10^{-15}
151	$CH_2CH(O)CH_2ONO_2 \rightarrow CH_2CHO + HCHO + NO_2$	3.1×10^{3}
152	$CH_2CH(ONO_2)CH_2O \rightarrow CH_2CHO + HCHO + NO_2$	3.0×10^{3}
	Aldehyde Reactions	
153	$HCHO + OH \rightarrow HCO + H_2O$	9.4×10^{-12}
154	$CH_2CHO + OH \xrightarrow{O_2} CH_2CO(O_2) + H_2O$	1.6×10^{-11}
155	$C_2H_2CHO + OH \xrightarrow{O_2} C_2H_2CO(O_2) + H_2O$	1.6×10^{-11}
156	$HCHO + NO_3 \rightarrow HCO + HNO_3$	1.8×10^{-15}
157	$CH_3CHO + NO_3 \xrightarrow{O_2} CH_3CO(O_2) + HNO_3$	2.0×10^{-15}
158	$C_2H_2CHO + NO_3 \xrightarrow{O_2} C_2H_2CO(O_2) + HNO_3$	2.0×10^{-15}

desired to include each and every important reaction occurring in the chemical system and to assign each the correct rate constant value. Failure to recognize the occurrance of an important reaction (e.g., PAN's thermal decompositions) or use of incorrect value of an important rate parameter (e.g. HO2+ NO) can lead to a model's predicted results to be questioned or even invalidated at some later time if the error is discovered by continuing research (44-47). Working out a specific model for each of the 50 or so major hydrocarbon constituents of polluted atmospheres is an onerous task. The propene model alone, which has been researched for over fifteen years, is still being improved or refined (48).

A compound specific model is validated by integrating the rate expressions on a large computer in a time consuming and expensive exercise. The computer simulation results are then compared with smog chamber results, changes made if necessary and the process repeated. The process of optimizing a model against many smog chamber runs is itself a tedious and imprecise exercise.

Since the development of explicit models for each hydrocarbon of atmospheric importance is a formidable task, some researchers have developed lumped or surrogate models. Although these approaches are based upon identical body of experimental chemical kinetic information, the way they treat hydrocarbon species differentiates them from each

other. In the lumped (generalized) approach, as its name implies, hydrocarbons are grouped either by classes (44,46,49-51), or by the types of carbon bonds (45,52-53). In lumping hydrocarbons, organic species are distributed into several classes such as alkane, alkene, aromatic and aldehyde and an average value of the OH rate constant is assigned to each class (44,46). This approach suffers from the fact that the rate constants for the reaction between hydrocarbon and free radical change significantly from one hydrocarbon component of the lumped case to the other, and also due to differences in hydrocarbon reactivity. The relative distribution of the hydrocarbons in each lumped class will vary throughout the photooxidation period such that the average value for the rate constants based upon the initial compositions can not reflect the reactivity of the lumped species at some later time. As a consequence, in order to compensate for that deficiency they had to adjust rate constants and stoichiometric coefficients for the lumped hydrocarbon/free radical reaction.

In the other approach, lumping by the type of carbon bond, organic species are partitioned by the similarity of their chemical bonds (45,52-53). Hydrocarbons are divided into groups of single-bonded carbon atoms, slow double bonds, fast double bonds, and carbonyl compounds. Because of the classification by reactivities of carbon bonds, the range of

the rate constants in a kinetic mechanism can be narrowed considerably when each carbon atom is treated according to its bond type.

The last modelling approach, surrogate models, can be thought of as an intermediate between explicit and lumped models. In this model organic species in a particular class are represented by one or more members of that class and the hydrocarbon chemistry is treated in a explicit fashion (54-55). An example of this case is the modelling approach used by EPA which is called EKMA (Emperical Chemical Kinetic Approach). This model is currently used to develop control strategies for emission in many areas of the United States. EKMA uses a mixture of propene and n-Butane plus a fairly explicit mechanism to simulate atmospheric processes occuring with far more complex mixtures (55).

Any of these modelling attempts have well recognized deficiencies. Single hydrocarbon models are fairly well developed in a few cases but in relative infancy for many hydrocarbons--in particular for aromatic hydrocarbons (56-57). Since they contain many reactions they are expensive to integrate on a computer. Lumped models which contain adjustable parameters are easier to use, less expensive to run, but doubt exists whether they can adequately explain smog chamber or atmospheric ozone formation.

Perhaps the most desirable approach (from the

standpoint of prediction) would involve an urban model which explicitly treats each important hydrocarbon. When combined with an accurate NOx model this would have the following important advantages:

1) Greater accuracy, since the model could be validated for each hydrocarbon constituent of the atmosphere separately.

2) Ability to incorporate long range transport since both high reactivity but rapidly disappearing and low reactivity long lasting hydrocarbons would be explicitly treated.

3) Ability to incorporate the effects of changing spectral distribution since major photolysis processes would be included explicitly (e.g. aldehyde photolysis).

4) Ability to accurately predict the effect of changing hydrocarbon composition without expensive revalidation against new smog chamber experiments. This would be a major advantage for many reasons: increasing use of aromatics for non-leaded gasoline; increasing use of diesel automobiles; switch to gasohol; modification of exhaust hydrocarbons by catalytic convertors which are more efficient in removing unsaturated hydrocarbons, impact of solvent emissions, etc. A model which explicitly treats each major hydrocarbon could routinely be modified for each case just by changing the source terms for each hydrocarbon.

The major difficulty of such a model would be that with

current methodology the model would be expensive and very time consuming to develop and very cumbersome and expensive to run since it would incorporate many hundreds of reactions. This research suggests a new approach to the development of a photochemical ozone model. The proposed simplified ozone model as is discussed in detail in Chapter III is based upon fundamental chemical kinetic constraints of the system. The model takes advantage of common features of the HC-NOx system to reduce the number of chemical species, while maintaining a high degree of detail and certain elements of chemical realism. The proposed model is constructed upon the concept of reactivity. This approach is utilized since the observed rate of hydrocarbon disappearance correlates closely with the OH rate constant, except for alkenes. Also, classification by hydrocarbon reactivity as suggested by Atkinson et al (36) correlates closely with the function of the individual hydrocarbon in converting nitric oxide to nitrogen dioxide and ultimately in the formation of ozone. In addition, since the reactivity of each organic species is almost constant in time, there is no need to adjust the stoichiometric coefficients for the reaction between hydrocarbons and free radical. In this model, each hydrocarbon would be represented by a source term and the ozone forming potential of the hydrocarbon as well as its oxidation products would be assessed separately. Further, product formation and loss

by OH reaction, product photolysis and dilution are handled explicitly. This mechanism has been tested against n-Butane/NOx and Propene/NOx data over a wide range of HC/NOx ratios. The results of model validation are presented in chapter VI.

CHAPTER III

MODEL FORMULATION: NO PHOTOOXIDATION

The initial desire has been to avoid a "brute force" approach to integration of tens or even hundreds of simultaneous differential equations. We have sought to develop the full kinetic potential for simplification which this chemical system may have. The proposed, simplified photochemical ozone model is based upon the most important reactions occurring. To achieve that goal, we inspected the rates of all elementary reactions produced by numerical integration of the detailed mechanism for propene and n-Butane (42,45). Inspection of the reaction mechanism reveals that many free radical reactions can be grouped according to their radical types. Therefore, to obtain a simplified scheme we eliminate reactions of lesser significance and lump reactions of similar types. These considerations led us to develop the simplified ozone model presented in table (II).

TABLE II

KINETIC FORMULATION OF THE SIMPLIFIED PHOTOCHEMICAL OZONE FORMATION

----->	NO	kNO	Emission rate
----->	HC	kHC	Emission rate
HC+OH----->	aRO2+P	k1	Hydrocarbon loss and Product formation.
P+OH----->	bRO2	k2	Product loss
P+hv----->	cRO2	kp	Product photolysis
RO2+NO----->	NO2	k3	
NO2+hv----->	NO+O	k4	Photostationary state
O+O2+M ----->	O3+M	k5	
O3+NO----->	NO2+O2	k6	
Everything----->	loss	kd	Dilution

This mechanism has the following essential features:

a) Source terms for nitric oxide and hydrocarbon, which make this model suitable for both smog chamber data and real atmospheric predictions.

b) Product formation and loss by reaction with hydroxyl radical.

c) Product photolysis.

d) NOx photolytic cycle and its perturbation due to the presence of hydrocarbon forming free radicals (RO2) capable of converting nitric oxide to nitrogen dioxide and ultimately forming ozone.

e) Dilution is explicitly treated by kd. This term can be made to include other loss processes for species which will be removed via wall loss, e.g. ozone.

f) Production of several effective conversions of NO--> NO2 via coefficients a,b and c. The coefficients a,b and c account for production of several intermediates, RO2 free radicals, which are capable of converting NO --> NO2. If we can evaluate experimentally the numerical values of these coefficients, in essence we have a simplified model that can predict how much ozone would be formed per destruction of hydrocarbon, since each time RO2 is formed, it is assumed to react with nitric oxide and convert it to nitrogen dioxide which leads to the formation of ozone.

From the above mechanism, the overall reactions in

terms of ozone formation are:

$$HC+OH \longrightarrow aRO2 + P \xrightarrow{aNO} aNO2 \xrightleftharpoons{h\nu, O_2} aO3 + aNO$$

$$P + OH \longrightarrow bRO2 \xrightarrow{bNO} bNO2 \xrightleftharpoons{h\nu, O_2} bO3 + bNO$$

$$P + h\nu \longrightarrow cRO2 \xrightarrow{cNO} cNO2 \xrightleftharpoons{h\nu, O_2} cO3 + cNO$$

An example will clarify the use of this simple model. The photooxidation of methane (CH4) would yield the following information on the number of ozone molecules formed per destruction of hydrocarbon and its product.

$$CH4+OH \longrightarrow CH3+H2O$$

$$CH3+O2 \longrightarrow CH3O2$$

$$CH3O2+NO \longrightarrow NO2+CH3O$$

$$CH3O+O2 \longrightarrow HCHO+HO2$$

$$HCHO+OH \longrightarrow H2O+HCO$$

$$HCO+O2 \longrightarrow HO2+CO$$

$$HCHO+h\nu \longrightarrow H2+CO$$

$$HCHO+h\nu \longrightarrow H+HCO$$

$$H + O2 \longrightarrow HO2$$

$$HO2+NO \longrightarrow NO2+OH$$

$$NO2+h\nu \longrightarrow NO + O$$

$O+O2+M \longrightarrow O3+M$

$NO+O3 \longrightarrow NO2+O2$

The overall reactions in terms of NO photooxidation are:

$$CH4 + OH \longrightarrow 2RO2 + HCHO \xrightarrow{2NO} 2NO2 \xrightarrow{h\nu, O_2} 2O3 + 2NO$$

$$HCHO + OH \longrightarrow RO2 + CO \xrightarrow{NO} NO2 \xrightarrow{h\nu, O_2} O3 + NO$$

$$HCHO + h\nu \longrightarrow 2\mathbb{Q}RO2 + CO \xrightarrow{2NO} 2\mathbb{Q}NO2 \xrightarrow{h\nu, O_2} 2\mathbb{Q}O3 + 2\mathbb{Q}NO$$

where $\mathbb{Q}$ is the quantum yield for radical production in HCHO photolysis. Therefore, by analogy to the simplified model a=2, b=1, c=2 and P=HCHO. This detailed mechanism is shown for methane only for sake of example and does not imply that methane (which reacts very slowly) is an important contributor to photochemical smog.

Assumption

In constructing the simplified NO photooxidation model the following assumptions have been utilized. First, it is assumed that hydrocarbon degradation is initiated by reaction with hydroxyl radical (OH). This is a good approximation since most hydrocarbon constituents of the polluted atmosphere are degraded by hydroxyl radical only. Only the alkenes react with ozone at rates somewhat slower than OH rates. However, since alkenes serve both as

sink for ozone (through reaction of alkene and ozone) and source for ozone (as a result of reaction and formation of RO2) the alkene-O3 reaction is not included in the simplified model formulation. The contribution of HC-O3 reactions to the overall model prediction will be discussed in chapter VI.

The second assumption includes treating the hydroxyl radical concentration as a model input rather than asking the model to predict its concentration. Although this approximation might seem severe it is quite justifiable. Most current smog chamber models, in order to explain the excess hydrocarbon removal rate, include an adjustable radical source term in their models. Carter et al.(58) and Atkinson et al.(59) have used a constant hypothetical wall source of OH radicals, and Hendry et al.(60) have assumed a similar input in the form of HO2. On the other hand, Fall and Seinfeld (44,46) and Whitten et al.(62-64) have assumed an initial presence of nitrous acid (HONO) formed heterogenously during loading of the smog chamber (65). Incorporating some free radical source terms for simulating smog chamber data is undoubtedly justifiable. The atmosphere itself may well have its own source term for free radicals due to presence of aerosols, surfaces, etc. However, the magnitude of the source term is determined by optimizing the model's output. We set [OH] to the value obtained from a semi-log plot of hydrocarbon decay as a

function of time, an equivalent but more straight forward approach. Finally, technology for measuring ambient OH is currently at hand so that actual measurements in urban and suburban atmosphere are likely (66-67). These measurements could then be used as a direct input for our model.

Third, we assume that all RO2 formed during the course of initial attack of OH on hydrocarbon, product degradation by OH, and product photolysis, will react with nitric oxide converting it to nitrogen dioxide and ultimately forming ozone. This is a very good approximation as long as NO > O3. The approximation may become invalid once nitric oxide is depleted and ozone starts to build up.

The simplified ozone model at this stage can accurately describe the NO-photooxidation regime. Once NO is completly oxidized to NO2 and ozone concentration reaches appreciable amounts, competing reactions such as O+NO2, ozone photolysis, NO2 +O3 and radical-radical termination reactions such as RO2+RO2, and RO2+NO2 must be considered. These reactions will provide direct or indirect removal paths for ozone. The contribution of these reactions to the overall model prediction are discussed in detail in chapter VI.

The simplified ozone model is similar in some respects to the pioneering work of Hecht and Sienfeld (H-S) in formulating the generalized chemical model presented in table (III). Although both approaches share the chemical

TABLE III

GENERALIZED H-S CHEMICAL MODEL

(1) $NO_2 + h\nu \longrightarrow NO + O$

(2) $O + O_2 + M \longrightarrow O_3 + M$

(3) $O_3 + NO \longrightarrow NO_2 + O_2$

(4) $O_3 + NO_2 \longrightarrow NO_3 + O_2$

(5) $NO_3 + NO_2 \xrightarrow{H_2O} 2HNO_3$

(6) $NO + NO_2 \xrightarrow{H_2O} 2HONO$

(7) $HNO_2 + h\nu \longrightarrow OH + NO$

(8) $CO + OH \xrightarrow{O_2} CO_2 + HO_2$

(9) $HO_2 + NO \longrightarrow NO_2 + OH$

(10) $HO_2 + NO_2 \longrightarrow HNO_2 + O_2$

(11) $HC + O \longrightarrow \alpha\ RO_2$

(12) $HC + O_3 \longrightarrow \beta\ RO_2 + \gamma\ RCHO$

(13) $HC + OH \longrightarrow \delta\ RO_2 + \epsilon\ RCHO$

(14) $RO_2 + NO \longrightarrow NO_2 + \theta\ OH$

(15) $RO_2 + NO_2 \longrightarrow PAN$

compactness in formulating the chemistry of the system, the H-S mechanism (44) differs from simplified in the following respects:

i) Contribution of the products of the HC-NOx photooxidation which further enhances the formation of smog is not included.

ii) Dilution is not included.

iii) [OH] is adjusted through reaction (14).

iv) Number of adjustable parameters (six) in H-S model are reduced to three rate parameters. Also, our mathematical approach differs significantly from H-S approach and most existing modeling approaches(57-64). In our approach rather than numerically integrate the rate expressions for every chemical species, we take advantage of the common features of the NOx photolytic cycle and its perturbation by hydrocarbon to minimize the required number of differential equations. We treat the HC/NOx system by explicit recognition of the fact that ozone formation is a continous process. This treatment simplifies our analysis and allows a system of differential equations to be reduced to a single differential equation which is solved analytically. This mathematical approach is presented in chapter IV.

At high HC/NOx ratios or high NOx concentration, contribution of termination reactions (RO2+RO2, RO2+NO2), competing

reactions with NO2 photolysis and termolecular formation of ozone (O+NO2) and the ozone removal paths (O3+NO2, O3+hv) become significant. The effect of these reactions in suppressing the ozone concentration are discussed in chapter VI. Our unique mathematical approach for estimating the ozone forming potential of a given hydrocarbon and its oxidation products are presented in the following chapter.

CHAPTER IV

MATHEMATICAL FORMULATION OF THE SIMPLIFIED OZONE MODEL

We now develop the simplified photochemical ozone model based upon the proposed mechanism. This will be done in several steps for clarity.

A. Relate hydrocarbon concentration to time:

The rate expression for hydrocarbon is

$$d[HC]/dt = kHC - k1[OH][HC] - kd[HC] \qquad (9)$$

Assume OH is constant at any level, including zero and define $k1[OH] = m\ (min)^{-1}$. Then $d[HC]/dt = kHC - (kd+m)[HC]$ and integration of this differential equation results in

$$[HC] = [HC]_o(\exp-(m+kd)*t) + (kHC)/(m+kd)*[1-\exp-(m+kd)*t)] \qquad (10)$$

where [HC] is the concentration of hydrocarbon at time (t) and $[HC]_o$ is its initial concentration. The above equation is strictly valid only if OH concentration is constant. However, other simplified versions could depict diurnal variation of OH.

B. Relate nitric oxide and ozone concentration to time:

Based upon the simplified mechanism, the rate expressions for NO and O3 are

$$d[NO]/dt = kNO - k3[RO2][NO] + k4[NO2][hv] - k6[NO2][O3] - kd[NO] \quad (11)$$

$$d[O3]/dt = k5[RO2][NO] - k6[NO2][O3] - kd[NO] \quad (12)$$

For the time being, we ignore the O+NO2 reaction, radical/radical termination reactions (e.g. RO2+RO2 and RO2+NO2) and degradation of hydrocarbon by its reaction with ozone. The contribution of termination reactions and the effect of the reaction of hydrocarbon with ozone is discussed in Chapter VI.

According to the photostationary equilibrium, the ozone concentration depends upon the ratio of [NO2]/[NO]

$$[O3] = (k4[hv][NO2])/(k6[NO])$$

Thus NO photooxidation and ozone accumulation represent a continuous process driven by RO2 radicals, even though O3 does not begin to build up until NO is gone.

Therefore, we define the difference between the NO and O3 concentration as a new variable, [NO-O3]. Some features of this treatment will be discussed shortly. This difference is obtained by subtracting differential equation (11) from

differential equation (12).

$$d[NO]/dt - d[O3]/dt = d[NO-O3]/dt \qquad (13)$$

Substitution of the nitric oxide and ozone rates gives:

$$d[NO-O3]/dt = kNO-k3[RO2][NO]+k4[NO2][hv]-k5[O][O2][M]-kd[NO-O3] \qquad (14)$$

Now, applying the steady state approximation for atomic oxygen [O] gives

$$d[O]/dt = k4[NO2][hv]-[O](k5[O2][M]+kd) =0$$

$$==> [O]=(k4[NO2])/(k5[O2][M]+kd)$$

and since k5[O2][M] >> kd, therefore

$$[O]= k4[NO2]/(k5[O2][M]) \qquad (15)$$

For peroxy alkyl we have

$$d[RO2]/dt = ak1[OH][HC] + bk2[P][OH] + ckp[P][hv] - [RO2](k3[NO]+kd) \qquad (15\text{-}a)$$

Making the steady state approximation for RO2 yields

$$[RO2] =(ak1[HC][OH]+bk2[P][OH]+ckp[P][hv])/(k3[NO]+kd). \qquad (16)$$

But m=k1[OH] and R=k2/k1, thus k2[OH] =Rm and finally

$$[RO2] = (a*m[HC]+b*R*m[P]+ckp[P][hv]) / (k3[NO]+kd)$$

Since $k3[NO] >> kd$ equation (16) can be reduced to

$$[RO2] = (a*m*[HC]+b*R*m[P])+ckp[P][hv]) / (k3[NO]) \quad (17)$$

When the steady state approximation for [RO2] and [O] are inserted back into equation (14) the following result is obtained.

$$d[NO-O3]/dt = kNO-m(a[HC]+bR[P])-cKP[P][hv] \quad (18)$$

This equation may be made time independent by dividing this differential equation by Eq.(9) to get

$$\frac{d[NO-O3]}{d[HC]} = \frac{kNO-m(a[HC]+bR[P]-ckp[P][hv]}{kHC-[HC](m+kd)} \quad (19)$$

The variable NO-O3 cancels out the photostationary equilibrium. For NO >> O3 the variable just equals NO and conversely, when NO << O3 it equals -O3. When NO=O3 the variable equals zero. For illustration, in figure (2) a typical smog photooxidation sequence is presented. In this figure we plot the normal variables: HC NO, NO2, and O3. In fig. (3) we plot the newly defined variable (NO-O3). The meaning of this variable is clear and its continious nature is apparent.

In order to solve the differential equation (19) we need to express P=P(HC) i.e, an equation which shows how product is

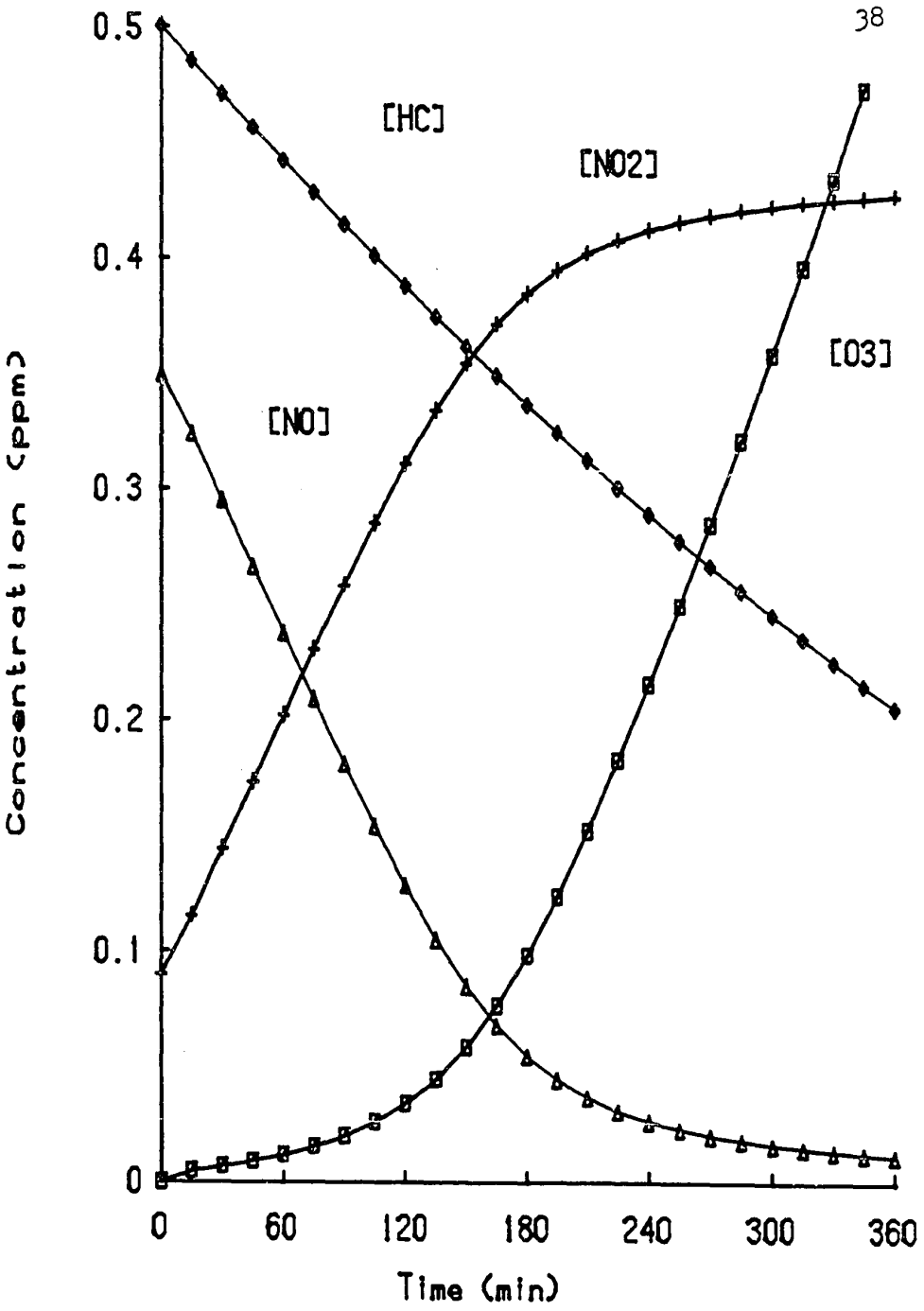


Figure 2. Typical smog photooxidation sequence.

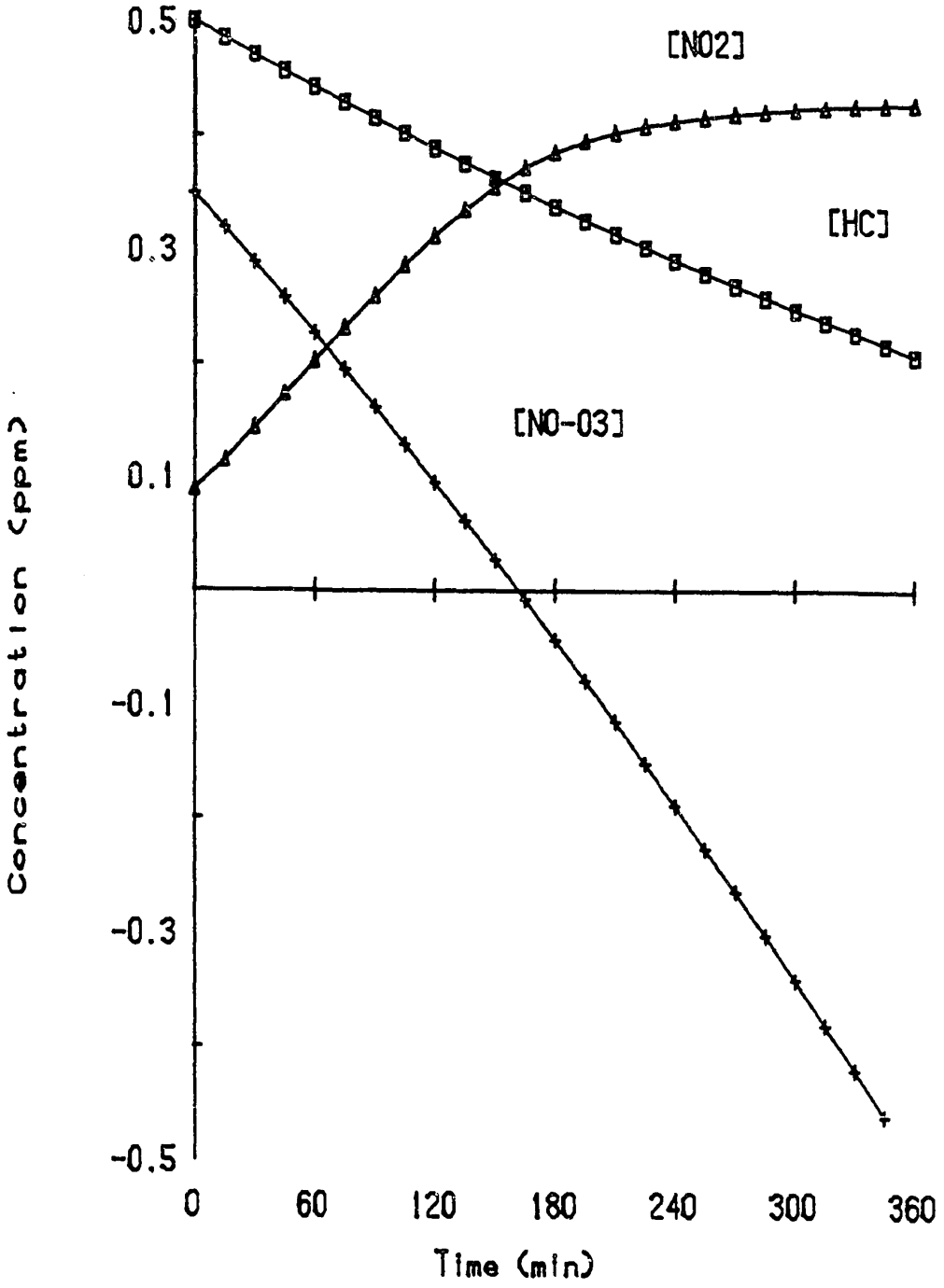


Figure 3. Newly defined variable for the photochemical smog system.

related to the precursor hydrocarbon. This information is obtained as follows:

C. Relate product to parent hydrocarbon concentration.

Here we show a simplified derivation for the case with no source term, no dilution, and no product photolysis. For this special case

$$d[HC]/dt = -k1[OH][HC] \qquad (20)$$

$$d[P]/dt = K1[OH][HC] - k2[OH][P] \qquad (21)$$

Now divide Eq. (21) by Eq. (20) to yield

$$d[P]/d[HC] = -1 + (k2/k1)*[P]/[HC] = -1 + R\ [P]/[HC] \qquad (22)$$

As before, the product to hydrocarbon OH rate constant ratio is defined as R. We integrate (22) to obtain

$$[P] = \{[HC]/(R-1)\} * \{(1-([HC]/[HC]_o)^{\frac{m(R-1)}{m+k_d}}\} \qquad (23)$$

This equation expresses [P] as a function of [HC] on a time independent basis. The time dependency may be brought back in at any time through Eq. (10). Figure (4) shows a plot of [P] vs. [HC] according to Eq. (23) for various values of R. The higher the value of R, the more reactive the product relative to parent hydrocarbon, and the sooner product reaches maximum concentration. However this maximum concentration is lower for higher values of R.

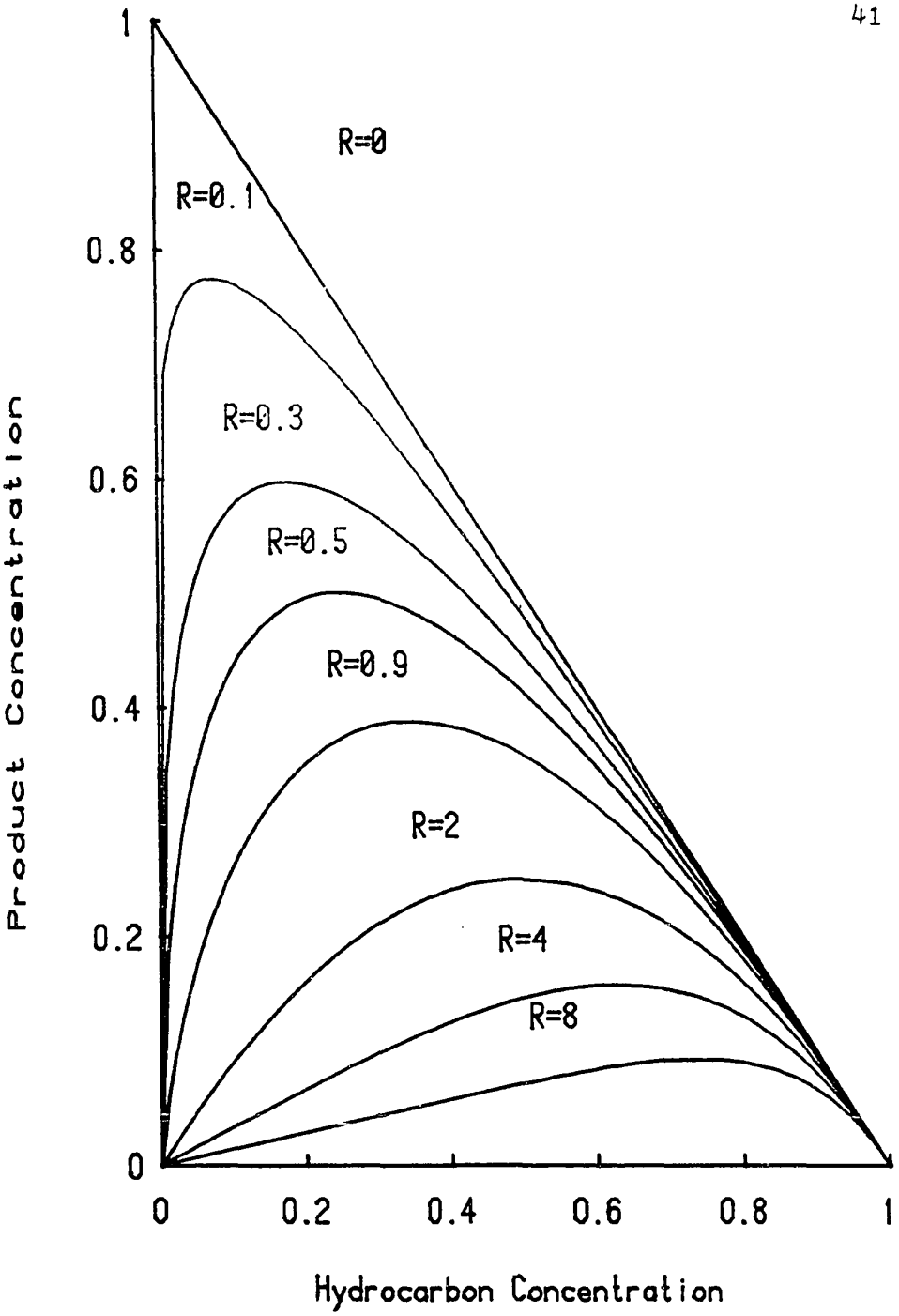


Figure 4. Graphical representation of product concentration vs. hydrocarbon concentration.

In the actual atmospheric case, source emissions of hydrocarbon and oxides of nitrogen, product photolysis, and dilution are all important. We may derive an expression similar to Eq. (23) for this case also if we assume OH is constant. The derivation is somewhat lenghty and only major steps toward the solution of this general case are presented. Considering the mechanism for the complete case we can show that

$$d[HC]/dt = kHC-[HC](m+kd)$$

$$d[P]/dt = m[HC] - [P](Rm+kp+kd) \qquad (24)$$

$$d[P]/d[HC]= (m[HC]-[P](Rm+kP+kd))/(kHC-[HC](m+kd)) \qquad (25)$$

In order to solve this differential equation knowledge of proper integrating factor is required. The following example illustrate the way by which integrating factor could be extracted from a given differential equation.

Considering the general form of first order linear differential equation

$$dy/dx + P(x)*y= Q(x)$$

Since $d/dx(y\exp^{\int P(x)dx}) = dy/dx\exp^{\int P(x)dx} + yP(x)\exp^{\int P(x)dx} = \exp^{\int P(x)dx}(dy/dx+yP(x))$

$p=\exp^{\int P(x)dx}$ is an integrating factor for the above differential equation and its primitive (general solution)

is

$$y\exp^{\int P(x)dx} = \int Q(x).\exp^{\int P(x)dx} dx + C$$

where C is constant of integration and its value is determined by the proper boundary conditions.

By analogy to the first order differential equation integrating factor for our system is $\rho = \exp^{\int \frac{Rm+k\rho+kd}{K_{Hc}-(m+kd)[Hc]} d Hc}$ and the primitive solution is

$$P = C \exp^{-\int \frac{Rm+k\rho+kd}{K_{Hc}-(m+kd)[Hc]} d Hc} + \left\{ \left(\exp^{-\int \frac{Rm+k\rho+kd}{K_{Hc}-(m+kd)[Hc]} d Hc} \right)\left(\int \exp^{\int \frac{Rm+k\rho+kd}{K_{Hc}-(m+kd)[Hc]} d Hc} . d Hc \right) \right.$$

$$\left. (m[Hc])(K_{Hc}-(m+kd)[Hc]) \right\} \qquad (26)$$

The integral in the right hand side of equation (26) was solved via integration by part ($\int udv = uv - \int vdu$) and constant of integration by assuming that at time = 0, [HC] = $[HC]_o$ and [P] = $[P]_o$ was obtained. The result (constant C) was then insertad back into Eq.(26) and the final equation is:

$$P = m \left\{ \frac{K_{Hc}-(m+kd)[Hc]}{(m+kd)^2-(m+kd)(Rm+k\rho+kd)} + \frac{K_{Hc}}{(m+kd)(Rm+k\rho+kd)} + \left[\frac{P_o}{m} - \frac{K_{Hc}}{(m+kd)(Rm+k\rho+kd)} \right.\right.$$

$$\left.\left. - \frac{K_{Hc}-(m+kd)[Hc]_o}{(m+kd)^2-(m+kd)(Rm+k\rho+kd)} \right] \left[\frac{K_{Hc}-(m+kd)[Hc]}{K_{Hc}-(m+kd)[Hc]_o} \right] \frac{Rm+k\rho+kd}{(m+kd)} \right\} \qquad (27)$$

The following constants are defined:

m = k1[OH]		min^{-1}
R = k2/k1		no unit
kd = dilution		min^{-1}
kHC = HC source		ppm/min
[HC]= initial hydrocarbon		ppm
[P] = initial product		ppm
kp = product photolysis		min

The solution of P=P(HC) , equation (27) was inserted back into equation (19) and we will drop the source term for HC and NO, (since we here consider only application of the model to smog chamber data) and for simplicity assume kp=0. This treatment resulted in

$$[NO-O_3] = [NO-O_3]_o [HC]_o^{-\frac{kd}{m+kd}} [HC]^{\frac{kd}{m+kd}} + \frac{m}{m+kd}[HC]^{\frac{kd}{m+kd}} \left\{ \frac{m+kd}{m}\left[HC^{\frac{m}{m+kd}} - HC_o^{\frac{m}{m+kd}} \right] \right.$$

$$\left. \left(a+\frac{bR}{R-1}\right) - \left(\frac{bR}{R-1}[HC]_o^{\frac{-m(R-1)}{m+kd}}\right)\left([HC]^{\frac{mR}{m+kd}} - [HC]_o^{\frac{mR}{m+kd}}\right)\left(\frac{m+kd}{mR}\right) \right\}$$

(28)

This analytical equation contains information on a, b and R where

a = (#O3 formed) / (HC destruction by OH)

b = (#O3 formed) /(product destruction by OH)

and R is a measure of the relative reactivity of the product of the initial OH reaction to that of its precursor hydrocarbon. If we plot [NO-O3] as a function of [HC] , the initial slope will be mainly determined by the value of a, and the final slope due to build up of the products is determined by a+b. The value of R is a manifestation of change in slope, i.e, measure of the curvature from initial to final slope. Ample examples of such plots are presented in chapter VI.

It was noticed that at high NO2 concentration, reaction of NO2+O becomes important and will compete with NO2 photolysis and termolecular ozone formation. This reaction acts as a sink for the removal of NO2 and O which both are assumed to form ozone. This reaction not only removes one molecule of NO2 and O, it also produces one molecule of NO which itself removes another molecule of ozone. Once this reaction was added to the model, we have to solve our differential equation numerically because of the appearance of the NO2 term in our final equation. The final equation under this condition is:

$$\frac{d[NO\text{-}O_3]}{d[HC]} = \frac{K_{NO} - K_3[NO][RO_2] + K_4[NO_2] - [O]\left\{K_5[O_2][M] - K_7[NO_2]\right\} - K_d[NO\text{-}O_3]}{K_{HC} - [HC](m + K_d)} \qquad (29)$$

where k7 is the rate constant for NO2+O reaction. In order to solve this differential equation, knowledge of an expression which relates nitrogen dioxide to precursor hydrocarbon is required, i.e., NO2 = NO2 (HC). This information was obtained from third order regression analysis by which we fit a polynomial to the experimental data and from its coefficients the desired equation was obtained. The result was then inserted back into the above differential equation which was solved numerically. The graphical representation of our numerical solution is presented in Chapter VI.

Also, it was observed that in the limiting case when we assume there is no dilution and no photolysis, equation (19) will be reduced to

$$d[NO-O3]/d[HC] = a + bR[P]/[HC] \qquad (30)$$

where

$$P = \{[HC]/(R-1)\}\{(1-([HC]/[HC]_o)^{R-1}\}$$

Notice that under this circumstance, the model becomes independent of OH concentration.

The result of expansion of $([HC]/[HC_o])^{R-1}$ according to the following equation

$$a^x = 1+x\ln a+(x\ln a)^2/2!+(x\ln a)^3/3! +.....$$

will be inserted into equation of [P] and the final result is:

$$d[NO\text{-}O3]/d[HC] = a - (b*R)\sum_{i=1}^{\infty}\frac{(R-1)^{i-1}}{i!}\ln(HC/HC_o)^{i} \qquad (31)$$

If the higher order terms of the expansion series can be left out, the model can be approximated with

$$d[NO\text{-}O3]/d[HC] = a - bR \ln (HC/HC_o) \qquad (32)$$

In this case the model's prediction depends only upon "a" and the product of "b" and R. For a detailed discussion of the accuracy and usefulness of this approximation, see Chapter VII.

It is worth while to mention some specific features of our treatment. First, it is clear from the differential equation (19) that the coordinate transformation, [NO-O3], and normalization of the rate expression with respect to hydrocarbon degradation by OH, i.e, (d[NO-O3])/dt /(d[HC])/dt results in a very useful ratio d[NO-O3] / d[HC], which is the net nitric oxide photooxidized per destruction of hydrocarbon. This equation contains the essential features and key elements of the nitric oxide photooxidation regime. This term in essence is a measure of the perturbation term discussed in the NOx photolytic cycle. Second, by normalizing the rate expressions and applying the steady state approximation for peroxy alkyl [RO2] and atomic oxygen [O] we removed the stiffness of the

differential equations and thus eliminate the traditional "Gear" numerical integration technique (68) utilized by most modelers for solving systems of differential equations. For our purpose a Euler numerical integration technique with optimized step size is sufficient (69). This feature eliminates the need for resorting to a large computer for solving systems of differential equations. All model computations can be done on any micro computer with about 2K RAM (random access memory) memory available. The model validation was done on a graphic desk top 4051 Tektronix mini computer. Third, by normalizing the rate expressions we eliminate the apparent presence of the variable time, we reduced the number of variables, while still implicitly retaining the time dependence. The model is thus very easy to use and the empirical parameters responsible for the chemistry of a given HC-NOx system (a,b,c,R) can be readily obtained by time independent analysis of the experimental data. Time dependency can be brought in at any time through denormalizing of the rate experessions.

CHAPTER V

EXPERIMENTAL PROCEDURES

V-a Smog Chamber Facilities

The reactions were carried out in an evacuable pyrex vessel (smog chamber) of 240 liter volume (Figure-5). The flask is spherical and was fitted with Viton O-rings and glass stainles-steel plug stopcocks. It is surrounded by a radio frequency (R.F) glow discharge net which is hooked up to a tesylcoil(Fisher Scientific coorporation). This high voltage generator was used to excite low pressure (~1 torr) gas discharge in the reaction vessel and connecting vacuum lines for clean up, a technique similar to that used in the semiconductor industry for cleaning substrates (70). This process served to remove condensed hydrocarbon products of previous experiments from the walls. Prior to each photochemical run the evacuable chamber was subjected to at least 3 hours of pumping at pressure below 10μ_m. The pressure of the smog chamber was determined by Pirani vacuum guage (GP-110). Also before each experiment the vessel was

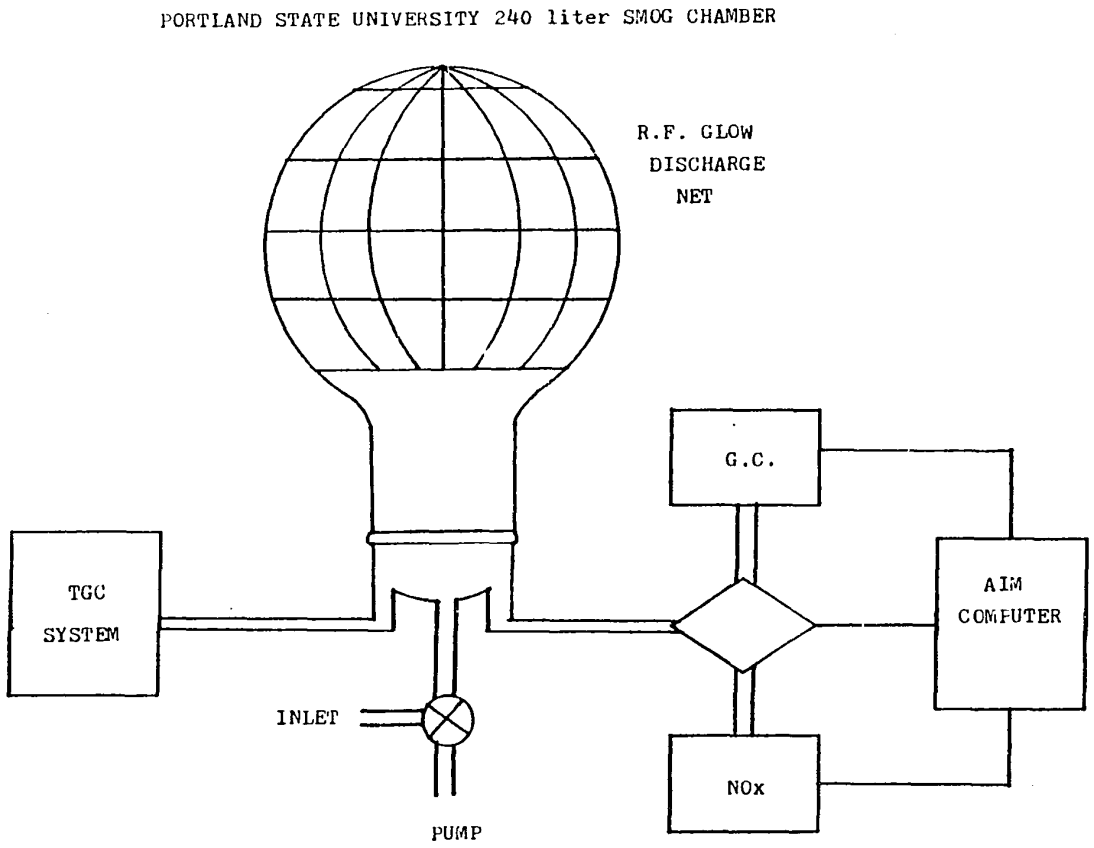


Figure 5. Portland state university smog chamber facilities.

routinely cleaned by the R.F. glow discharge at pressure of about 1 torr of zero air (Airco). After the pumping and cleaning procedures, the flask was filled with zero air to about 25 torr above atmospheric pressure. The overpressurized system allows sample withdrawal under positive pressure and prevents inward leaks in the sample withdrawal system which would cause dilution. The background concentration of hydrocarbon was monitored by gas chromatography (GC) and was checked with another GC which measures CO, CO2, and total gas phase carbon (TGC). Fig (6) is a schematic representation of the TGC system. The total gas phase measurements were determined by passing the sample over an oxidative catalyst heated up to 923K (71). This oxidized all hydrocarbons and carbon monoxide to CO2, which was then measured quantitatively by gas chromatography. The total carbon analysis was calibrated quantitatively by pressure/volume expansion into 240 liter smog chamber. For a detailed discussion of the total gas phase carbon measurements refer to the paper by O'Brien et al (72).

The flask was irradiated with 48 fluorescent lights to simulate the ultraviolet portion of the solar spectrum. The flask had an equal combination of fluorescent black (GE-F40-BL) and fluorescent sun (GE-F5-40) lamps. The light intensity produced within the reaction vessel is comparable to that of tropospheric sunlight in its ability to photodissociate NO2 but falls off more rapidly in intensity

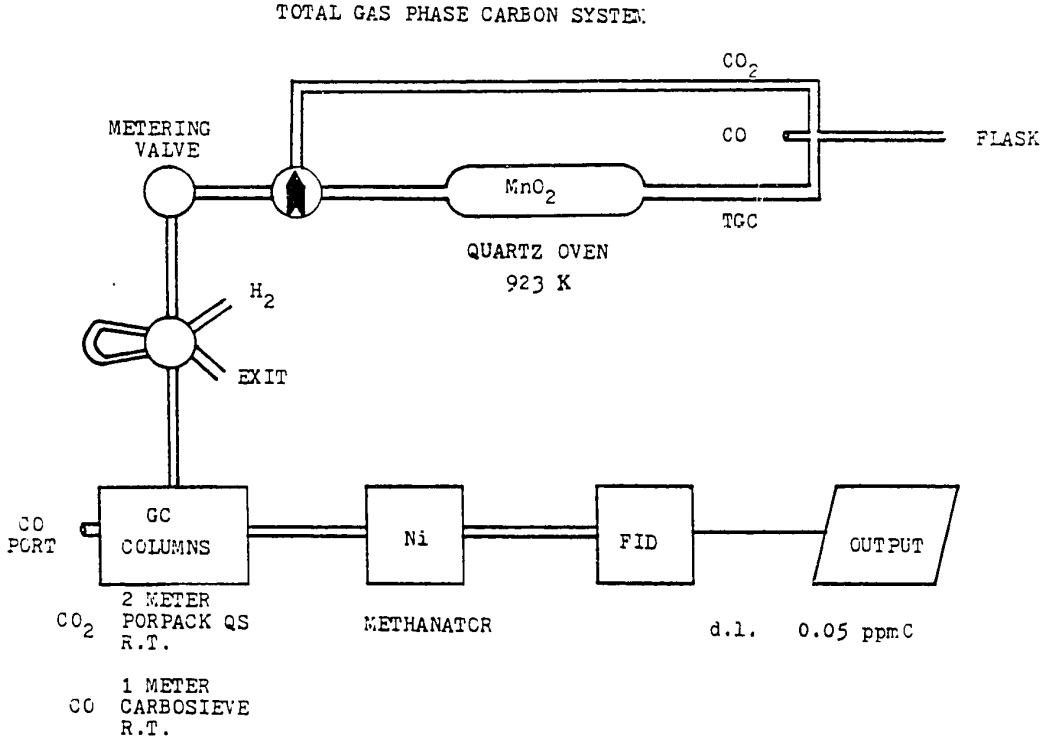


Figure 6. Schematic representation of total gas phase carbon measurement.

at shorter wavelenghts.

V-b Light Intensity Measurements

Light intensity measurements were accomplished by the procedures recommended by Holmes et al (73). In this technique the rate constant for NO2 photolysis (k1) is determined in a nitrogen atmosphere. The value of k1 is calculated from the following equation (assuming that no oxygen is present).

$$k_1 = \frac{1}{2\Delta t}\left\{(1+R_1-R_2)\ln\frac{[NO_2]}{[NO_2]_o} + R_2\left[\frac{(NO_2)_o}{(NO_2)} - 1 + [NO]_o\left(\frac{[NO_2]_o-[NO_2]}{[NO_2][NO_2]}\right)\right]\right\} \qquad (33)$$

where Δt= t(final)-t(initial), R1 = k5[M]/k4 and R2 = k7[M]/k4 and ks are the rate constants corresponding to the reactions presented in table (IV). Values for R1 and R2 were taken to be 0.26 and 0.16, respectively, as recommended by Holmes etal (73).

Briefly, the general experimental procedures for actinometry experiments are as follows. A premeasured concentration of NO2 is delivered into the evacuated and cleaned chamber. Then the flask is filled with 99.995% nitrogen to about 1 atmosphere. After initial NOx readings are determined, the light is turned on and the progress of the reaction, i.e., photolysis of NO2 was monitored. No

TABLE IV

HOLMES ET AL (73) MECHANISM FOR NO2 PHOTOLYSIS RATE CONSTANT

(1)	$NO_2 + h\nu \longrightarrow NO + O$	k1
(2)	$O + O_2 + M \longrightarrow O_3 + M$	k2
(3)	$O_3 + NO \longrightarrow NO_2 + O_2$	k3
(4)	$O + NO_2 \longrightarrow NO + O_2$	k4
(5)	$O + NO_2 + M \longrightarrow NO + O_2$	k5
(6)	$NO_3 + NO \longrightarrow 2NO_2$	k6
(7)	$O + NO + M \longrightarrow NO_2 + M$	k7
(8)	$2NO + O_2 \longrightarrow 2NO_2$	k8
(9)	$NO_3 + NO_2 \longrightarrow N_2O_5$	k9
(10)	$N_2O_5 \longrightarrow NO_3 + NO_2$	k10
(11)	$NO_2 + O_3 \longrightarrow NO_3 + O_2$	k11

initial warm up period for our light sources was needed. This feature can be seen in fig (7). Fairly constant voltage across a photo resistor (measured by HP-425- A DC micro voltmeter) was indicative that the light source did not change its intensity with time.

Graphical representation of equation (33) is illustrated in figure (8). In that figure the right hand side of equation (33) which is abbriviated with Z5 is plotted vs. time. From the slope of that plot, the photolysis rate constant was calculated. The overall light intensity measurement gave an NO2 photolysis rate of 0.18 min^{-1}.

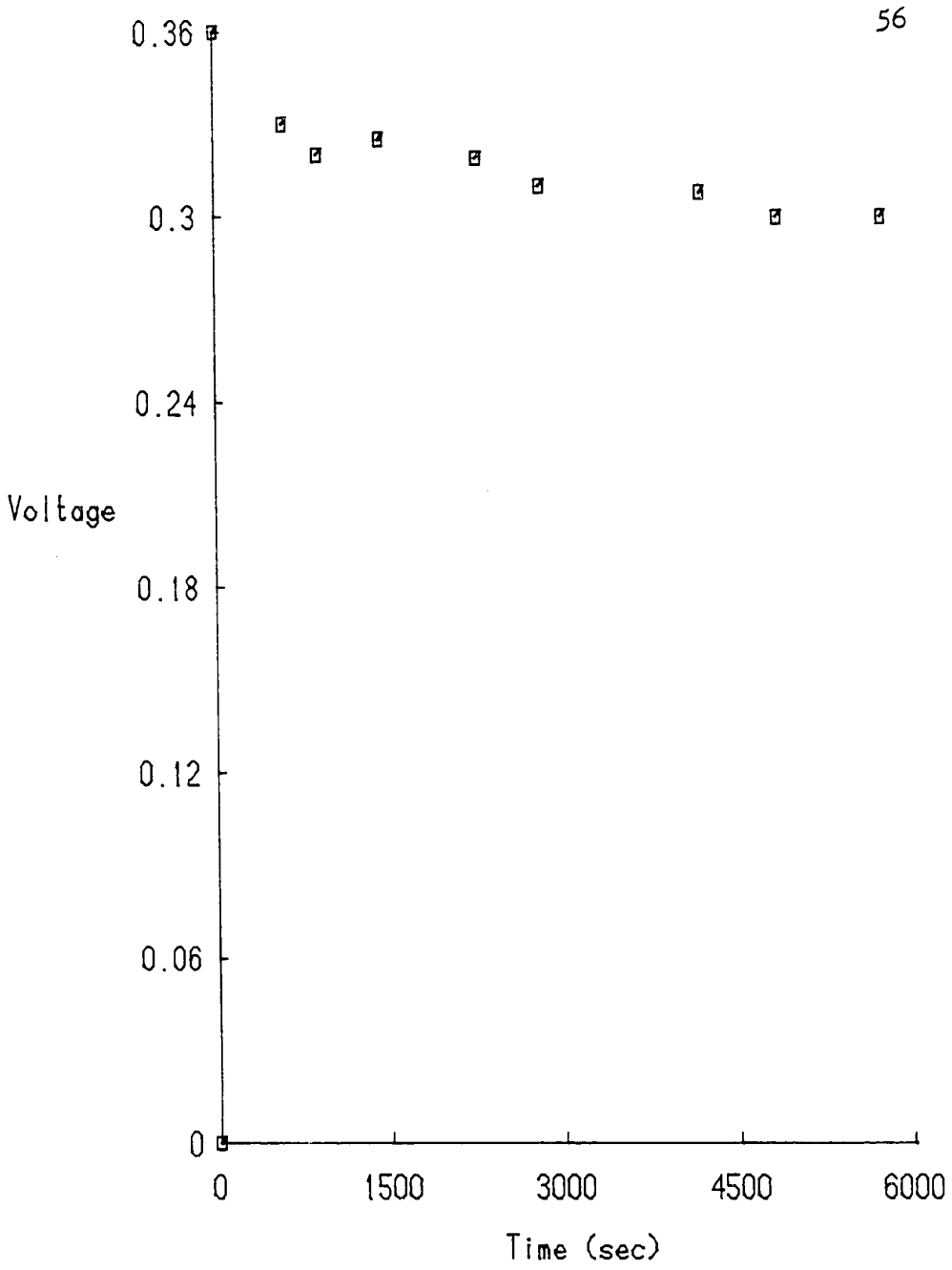


Figure 7. Variation of voltage by irradiation time.

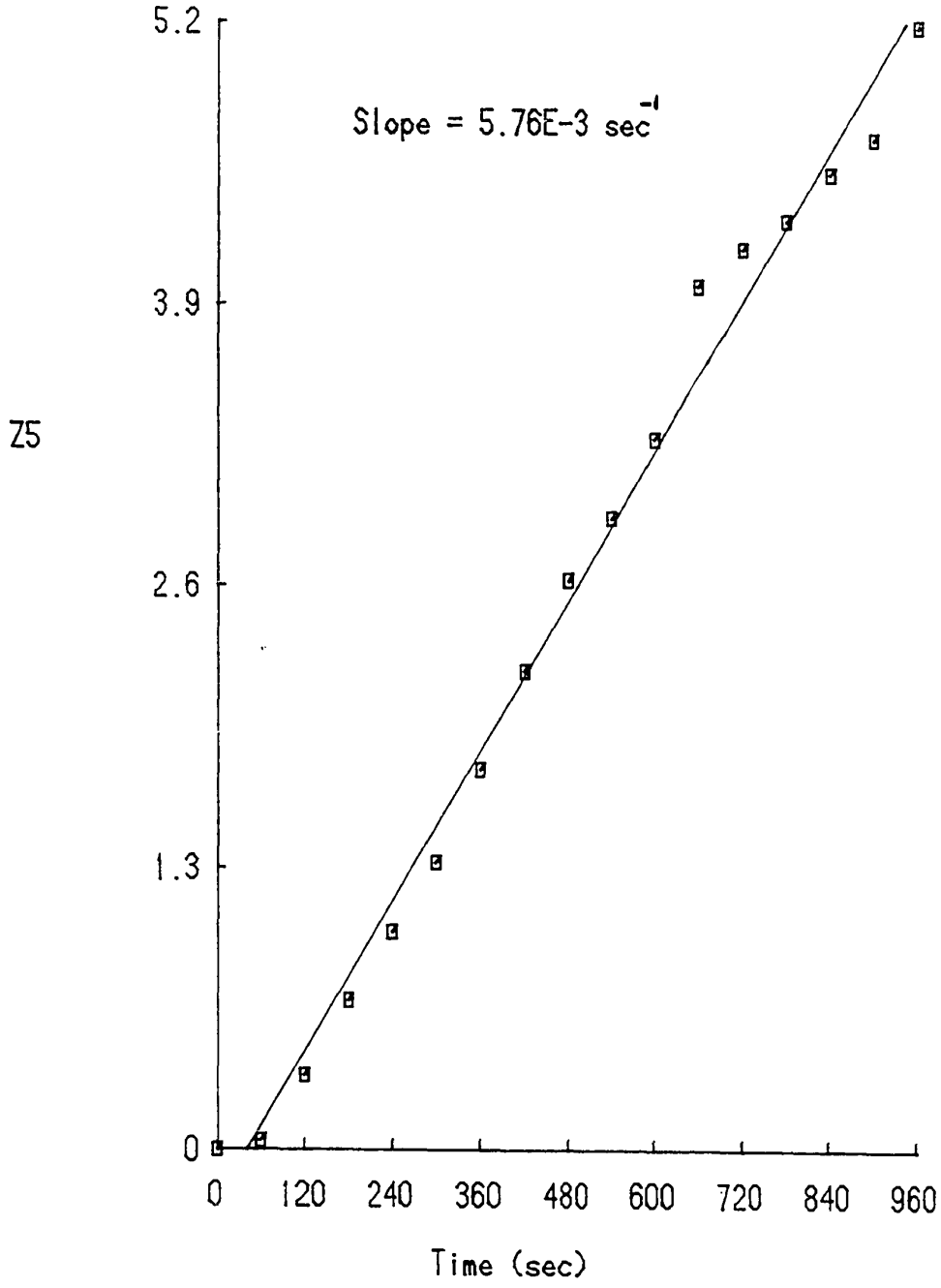


Figure 8. Actinometry experiment; NO_2 photolysis.

V-c Sampling System and Analytical Techniques

Primary pollutants (oxides of nitrogen (NOx) and hydrocarbon HC), were prepared in a seperate vacuum line which is equipped with oil manometer. Samples were collected in small pyrex flasks with volume ranging from 2cc to 40cc. The small flasks were fitted with Viton O-rings and teflon plug stopcocks. The premeasured nitric oxide and hydrocarbon were delivered through 2 seperate inlet ports to the 240 liter flask. Once the flask was partially filled with zero air to about 300 torr, a measured volume of liquid water sufficient to give 3.5E+17 cm^{-3} was injected by a syringe through a seperate inlet port into the flask. This correspond to 38% relative humidity for reaction temperature which was 300.0±2.0 K. The pressure of the system was brought to 800 torr with zero air and was monitored during loading by a Wallace & Tiernan model FA-160 pressure gauge. This charging procedure, i.e. admitting reagent gases into the evacuated chamber, followed by filling with zero air, allowed for a complete mixing.

The sample line which extends to the middle of the smog chamber leads to an automatic sampling device which is controlled by Rockwell Aim-65 microprocessor. The automatic sampler has two modes of operation, sampling and injection. By executing a basic language computer program the sampling parameters are initialized. Parameters included time

interval between each sample, sampling duration, time for gas chromatography door to remain open after injection for optimized peak resolution, and slope setting for peak area evaluation. The listing of the basic program is presented in appendix (A). For a detailed discussion of interfacing the GC with Rockwell Aim-65 see paper by Chan etal (74).

In the sampling mode, oxides of nitrogen were measured by a chemiluminescent NOx analyzer. In this mode after a certain amount of time as instructed in the basic program, the sampler automatically shifted from NOx to NO mode and the difference gives the concentration of nitrogen dioxide. Under the experimental conditions used i.e., low HC/NO, the contribution from other nitrogen compounds such as PAN and other nitrates is negligible and no corrections were required. The chemiluminescent reaction of nitric oxide and ozone is the heart of Thermo electron's model 12A NOx analyzer used. This instrument allows fast and accurate measurement of nitric oxide with eight linear full-scale setting, ranging from 0.01 ppm up to 1000 ppm.

To measure nitric oxide concentration, the gas sample to be analyzed is blended with ozone in a flow reactor. The chemiluminiscence results from the following rection

$$O3 + NO \text{ -----> } O2 + NO2 + h\nu$$

and is monitored by a photomultiplier tube positioned at one end of the reactor. Light emission results when

electronically exited NO2 molecules revert to their ground state.

To measure NOx concentrations the sample gas flow is diverted through an NO2-to-NO convertor. The chemiluminescent response in the flow reactor to the convertor effluent is linearly proportional to the NOx concentration entering the convertor.

During the NOx sampling period, the hydrocarbon constituents are passed through a 20 cc glass loop. The contents are then automatically injected into the GC (Perkin-Elmer 990) which is equipped with a flame ionization detector. Table (V) contains optimum experimental conditions utilized for the various hydrocarbons studied by gas chromatography. Collected experimental data are then stored on magnetic tapes and were analyzed with Tektronix 4051 minicomputer. Results of our smog chamber experiments are presented in chapter VI.

TABLE V

OPTIMUM EXPERIMENTAL CONDITIONS FOR COMPOUNDS STUDIED

Compound	GC Column	Column temp (C)	Time GC door after inj.
Propene	Propak QS	130	2
n-Butane	Propak QS	90	5
Hexane	Propak QS	80	4
Toluene	SP-2100	70	6
Acetaldehyde	Propak QS	60	8
CO	Carbocieve S	room temp	2
CO2	Propak QS	room temp	2

CHAPTER VI

MODEL VALIDATION

VI-a Application of model to smog chamber data

In chapter IV we developed a general equation, Eq.19, which relates the net rate of NO-photooxidation to several important parameters. That equation on a functional basis can be reduced to

$$d[NO\text{-}O3]/d[HC] = f(kHC,kNO,kd,kp,a,b,c,R,m) \quad (34)$$

The first four variables, the source terms for hydrocarbon and nitric oxide, and the dilution and photolysis rate constants are functions of particular geographic and meterological situations for real atmospheric conditions. The next four variables are functions of the particular hydrocarbon in question, its reactivity and the reactivity of its oxidation products. The last variable, m, combines the hydrocarbon's reactivity with the local OH concentration. It is the latter five variables which one commonly wishes to observe, directly or indirectly, in a smog chamber experiment. Normally this is done by

formulating an explicit mechanism for the hydrocarbon in question and then validating the mechanism via computer integration against smog chamber data. This method, while traditional and theoretically the most accurate course to follow, is time consuming, expensive, unwieldy and difficult to assess in terms of true accuracy. The equation developed in chapter IV suggests a different and in some respect more straightforward approach. We may begin this approach by observing some experimental data plotted in a time independent mode, (NO-O3) vs. (HC). The advantage of such a plot is that it can be applied in a straightforward fashion to many experiments. The slope of such a plot as mentioned in chapter III is then related to the number of NO molecules photooxidized per destruction of hydrocarbon. The change in slope from initial to final values is manifestated in the value of R, a direct measure of the relative reactivity of product to precursor hydrocarbon.

In order to examine the validity of our model and its underlying assumptions, the model was tested against the n-Butane/NOx and Propene/NOx systems over a wide range of HC/NOx ratios. These two hydrocarbons were chosen because they have been extensively studied in the past, they provide a very good data base, and their detailed mechanisms are fairly well established (39-42,52-54). The data base for our model validation was provided mainly by the State-Wide Air Pollution Research Center (SAPRC) of the University of

California, Riverside UCR , (75-76) and by the University of North Carolina (63). In addition to the ample existing literature data, at Portland State University we have conducted some experiments in our 240 liter glass smog chamber to establish an outside reference and to perform experiments in the region where there are not many data available (i.e. low HC/NO ratios). This region is the most useful for validation of our mechanism, even though these ratios do not normally occur in ambient air.

VI-b Application of model to n-Butane/NOx smog chamber data

We began our model validation by applying Eq. (29) to the n-Butane/NOx experimental data. In Figure (9) we plot [NO-O3] vs. [n-Butane] for UCR run EC-304. Point A on the figure corresponds to the initial experimental concentrations (time=0). The progress of time is implicitly represented by the direction of the arrow. As time progresses, the concentration of the primary pollutants (NO, HC) declines and the concentration of the secondary pollutants (e.g. ozone) builds up. Thus the reaction progresses in the direction of the arrow from the positive region (NO photooxidation) to the negative region (ozone accumulation). We applied Eq. (29) to fit as closely as possible the behavior of the experimental data. The best fit to the experimental data was obtained for the value of a=1.9, b=4 and R=1.1 which is shown by solid line in Figure (10). The hydrocarbon reactivity (m) for that experiment was obtained from a semi-log plot of n-Butane vs. time Fig. (11). The hydrocarbon reactivity is determined from the slope of such plot, by subtracting the dilution rate due to sampling. The constant slope of such a plot is in agreement with the assumed constant concentration of hydroxyl radical. Further examples of the time independent plots for the n-Butane/NOx system are presented in Figures (12-19) and

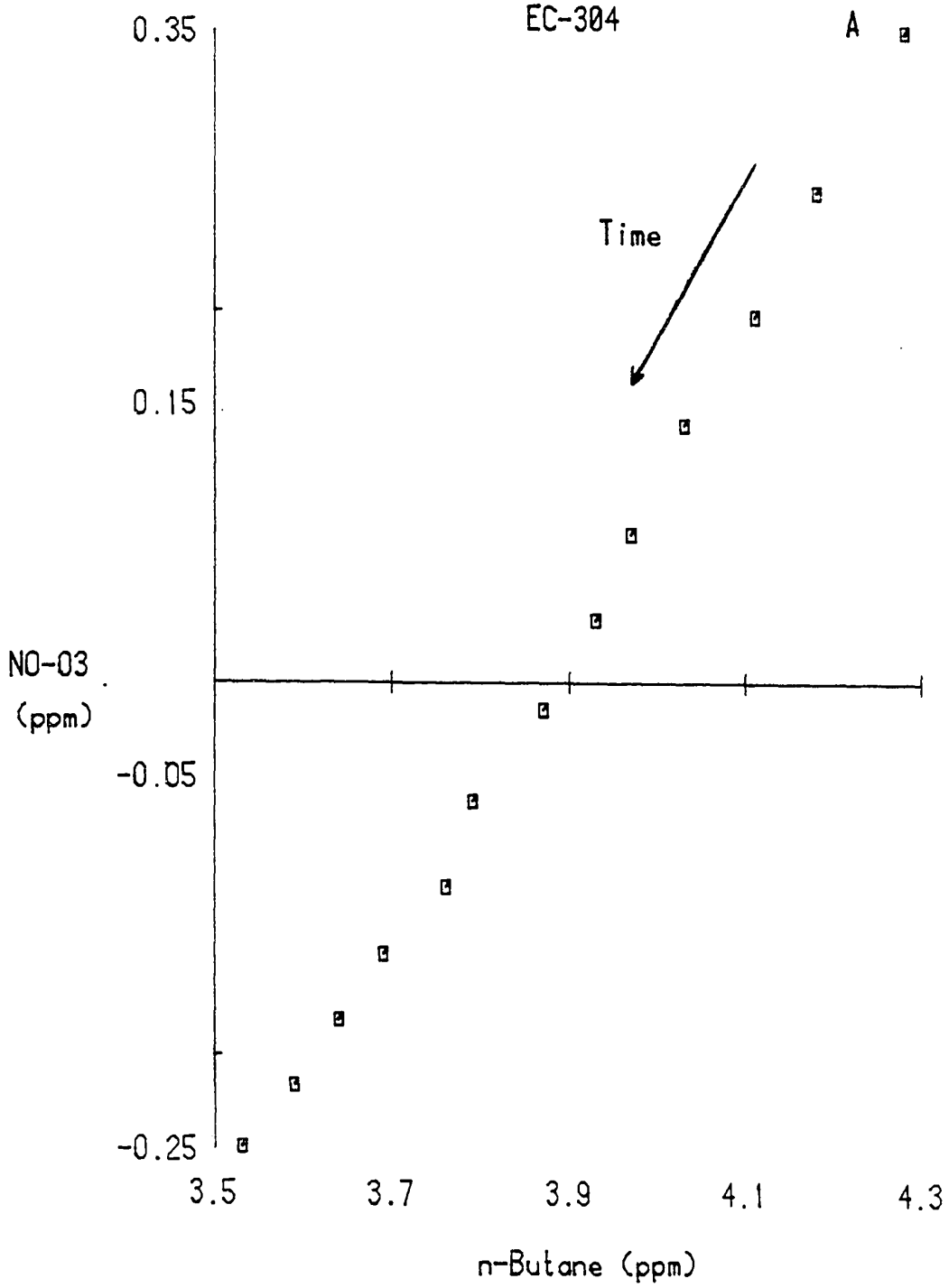


Figure 9. [NO-03] vs. [n-Butane] for EC-304.

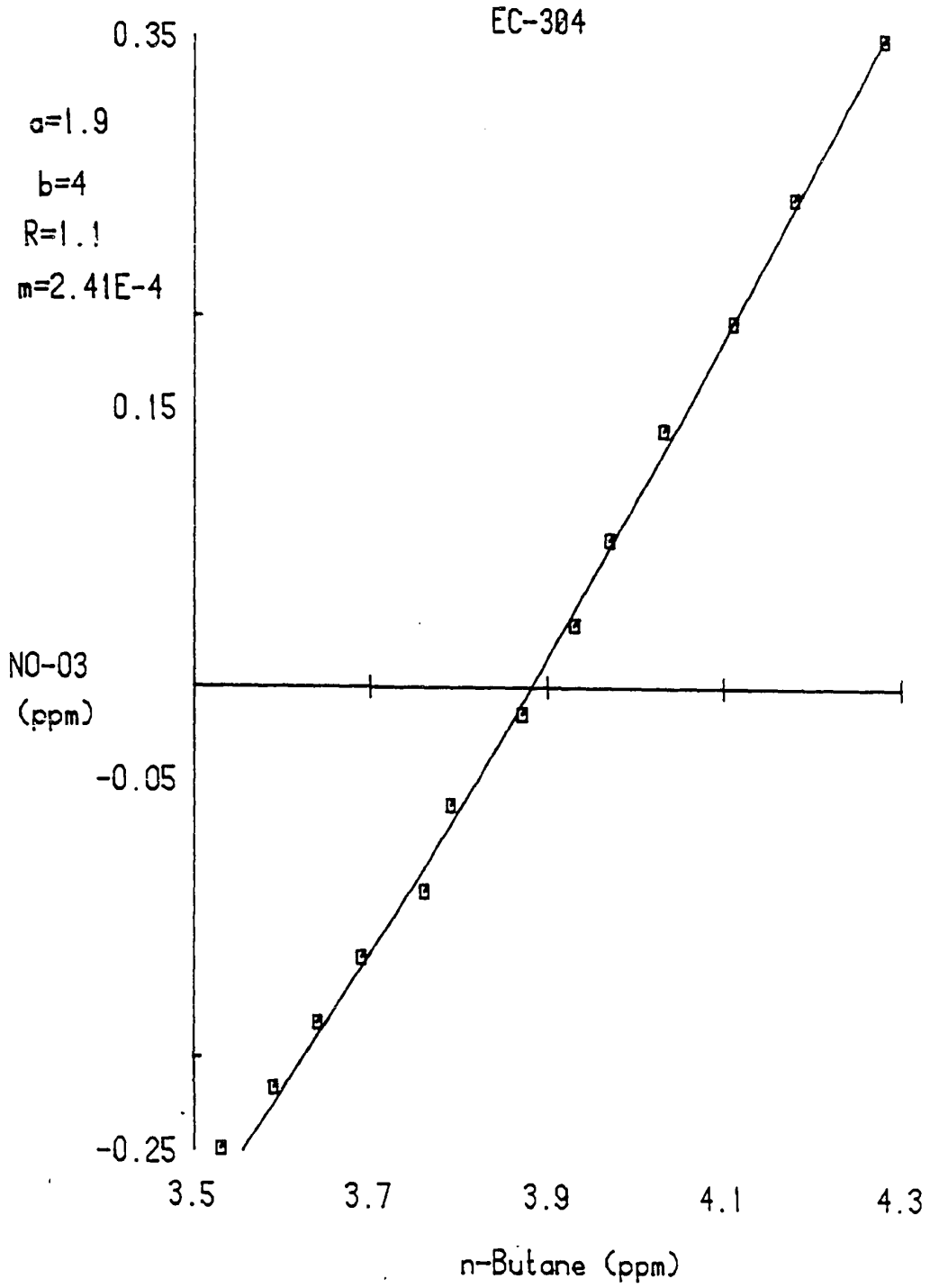


Figure 10. Simplified model prediction for EC-304.

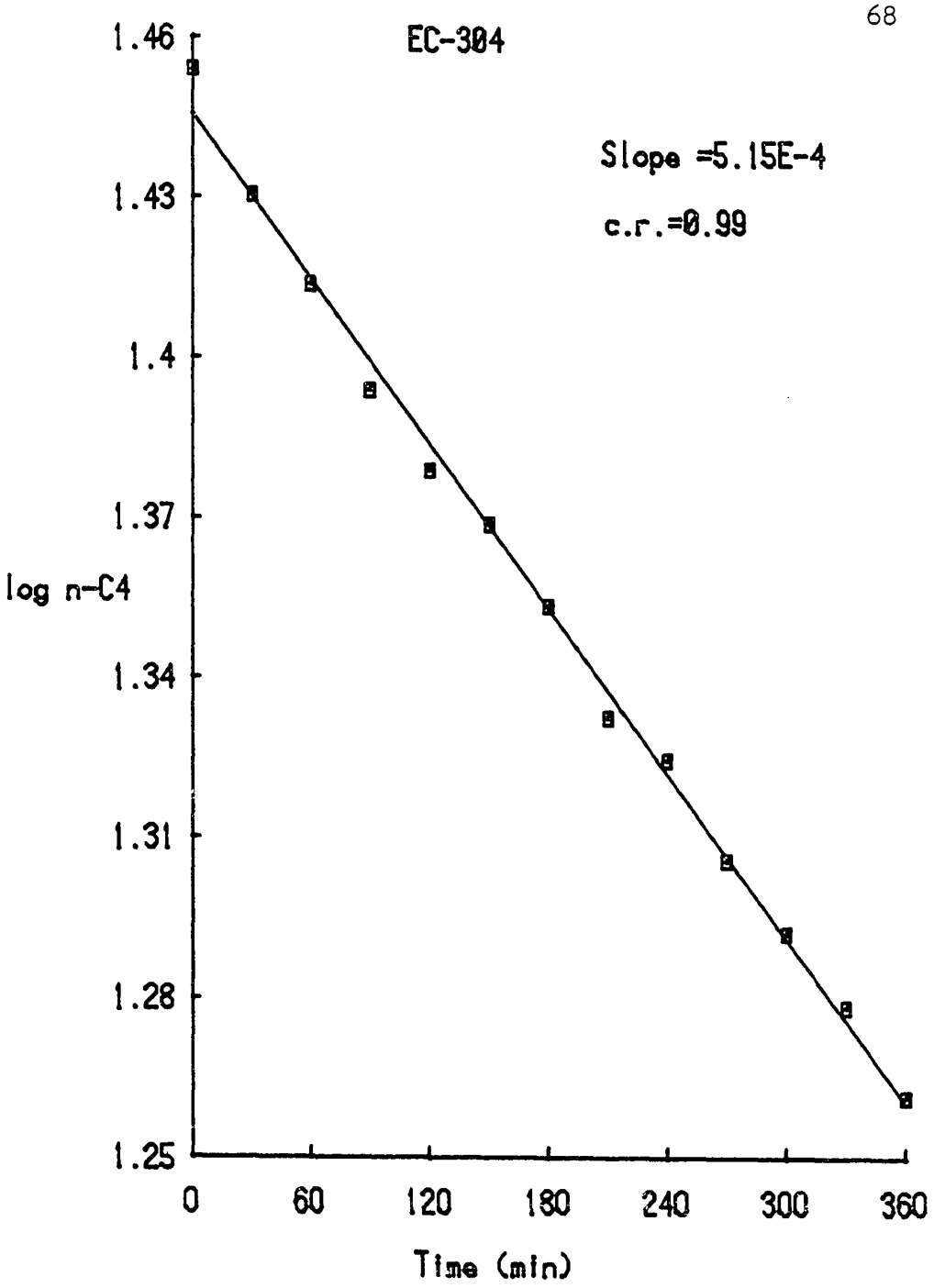


Figure 11. Hydrocarbon's reactivity for n-Butane EC-304.

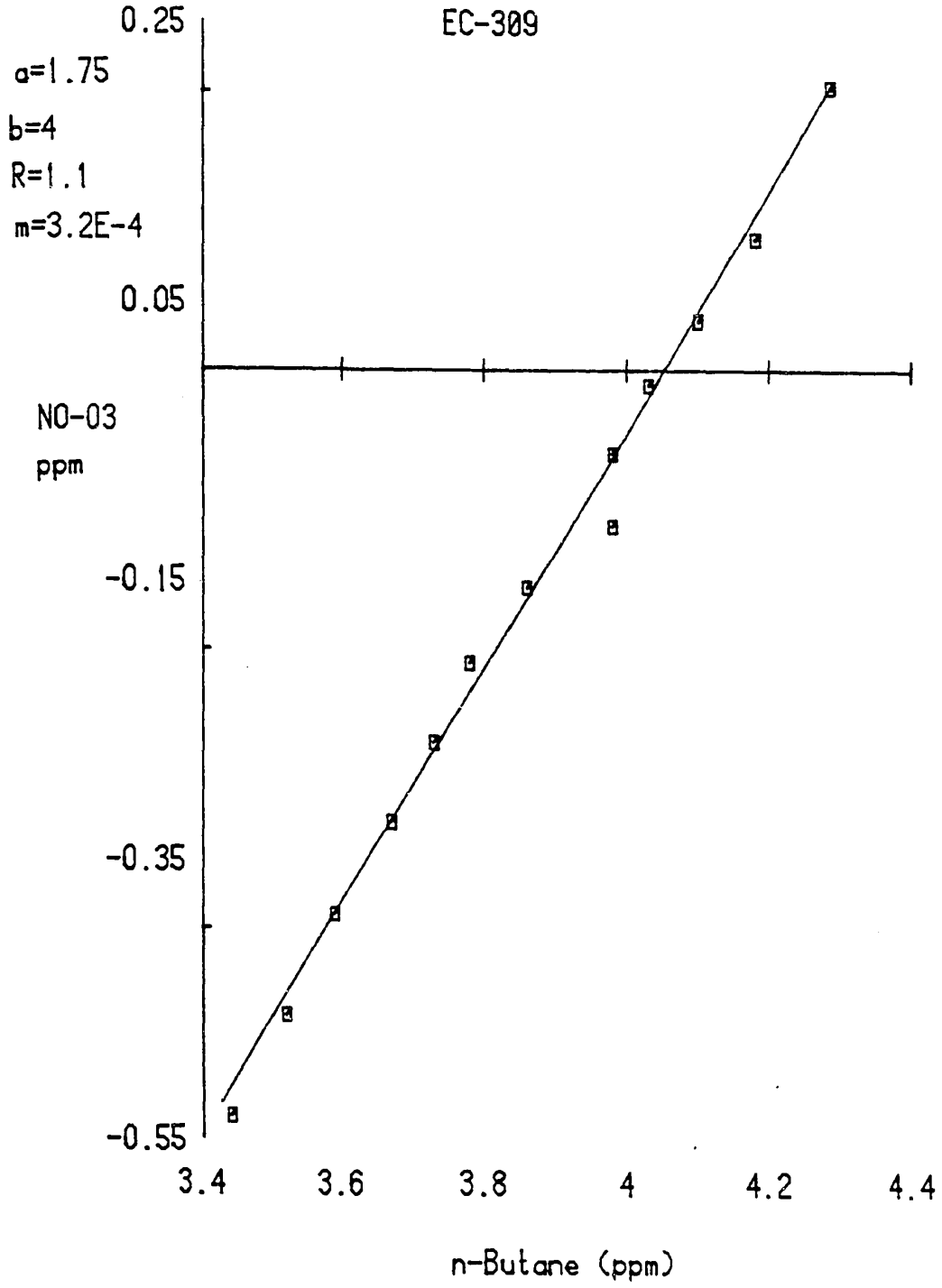


Figure 12. Simplified model prediction for EC-309.

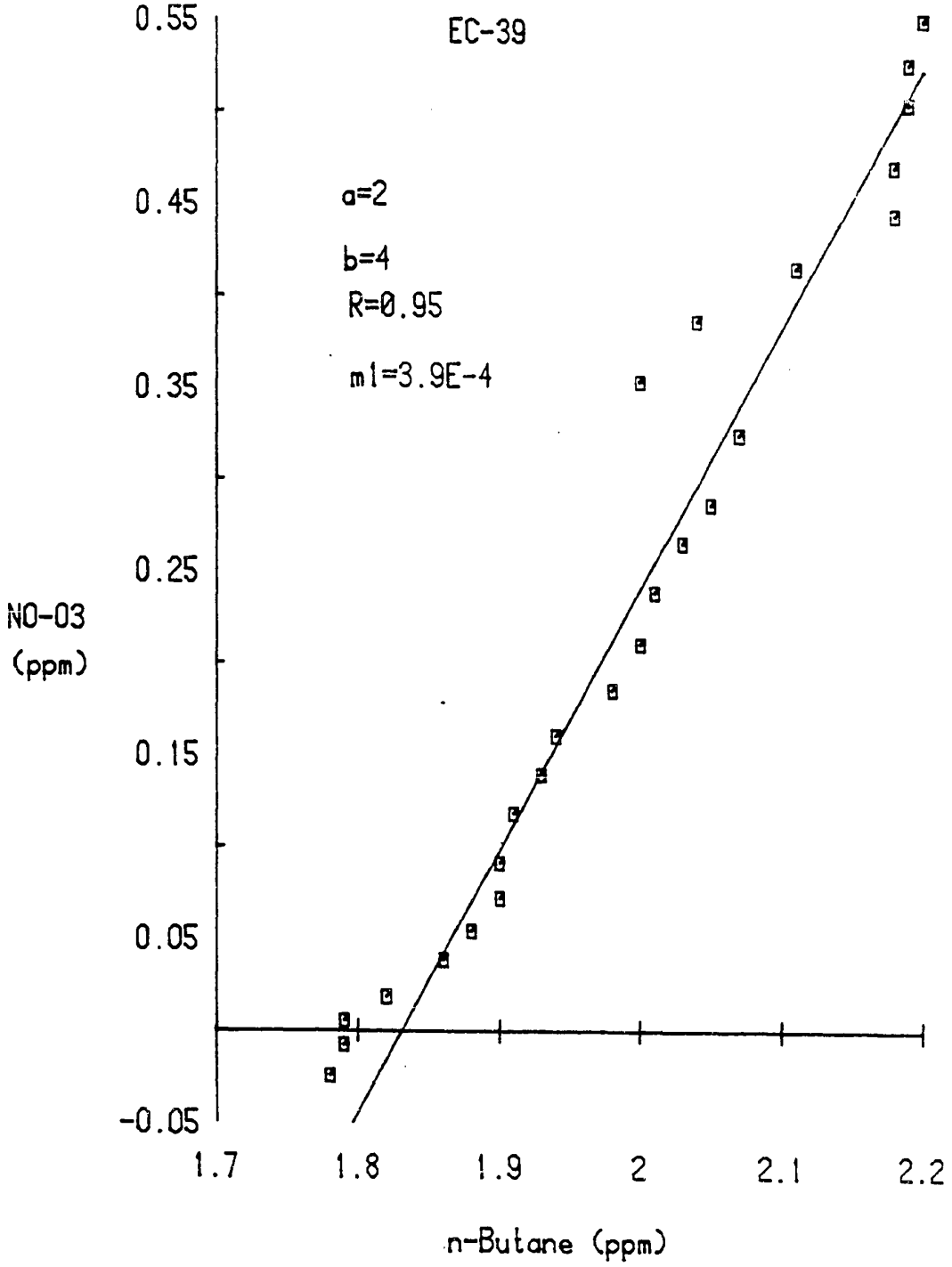


Figure 13. Simplified model prediction for EC-39.

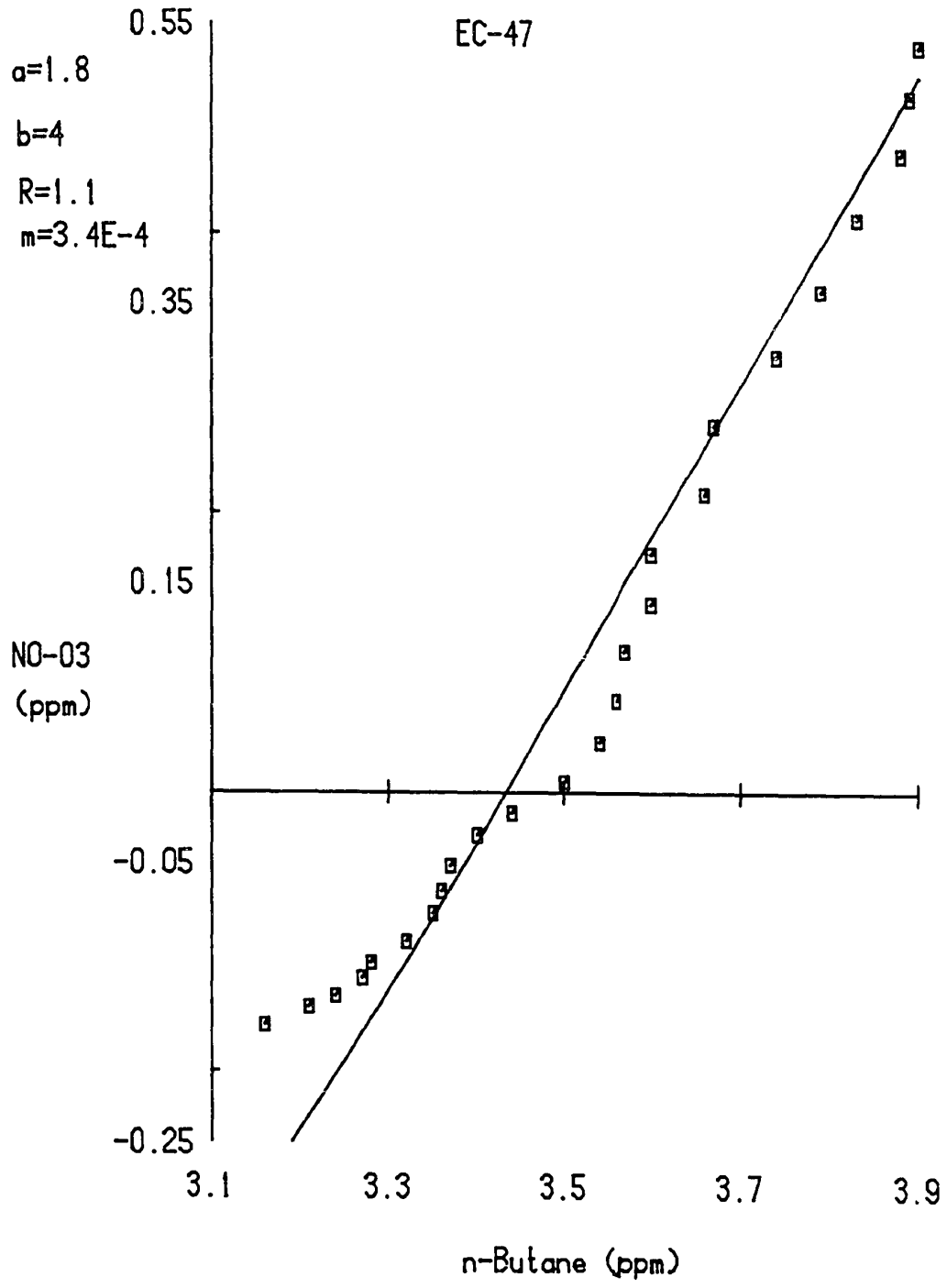


Figure 14. Simplified model prediction for EC-47.

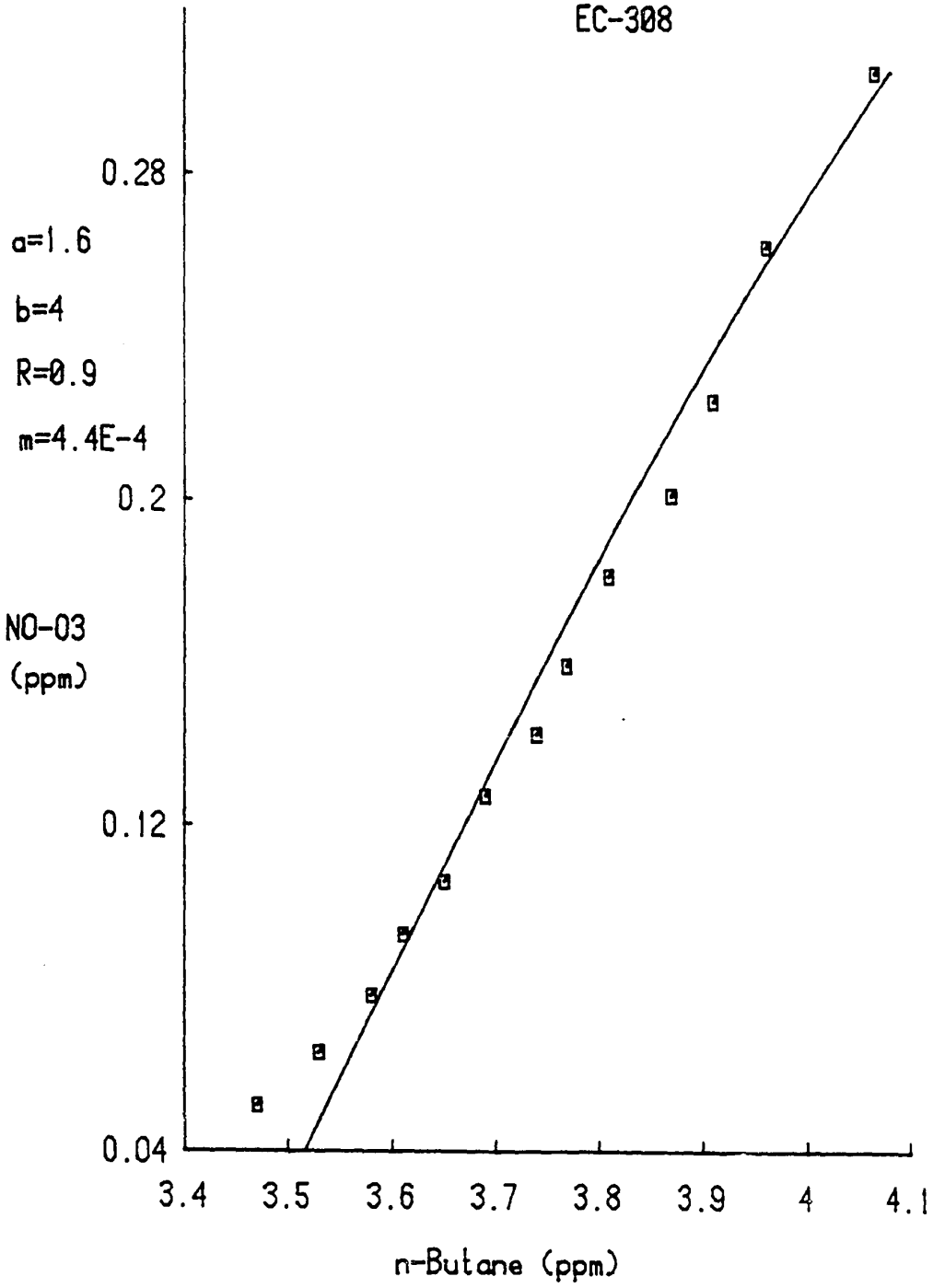


Figure 15. Simplified model prediction for EC-308.

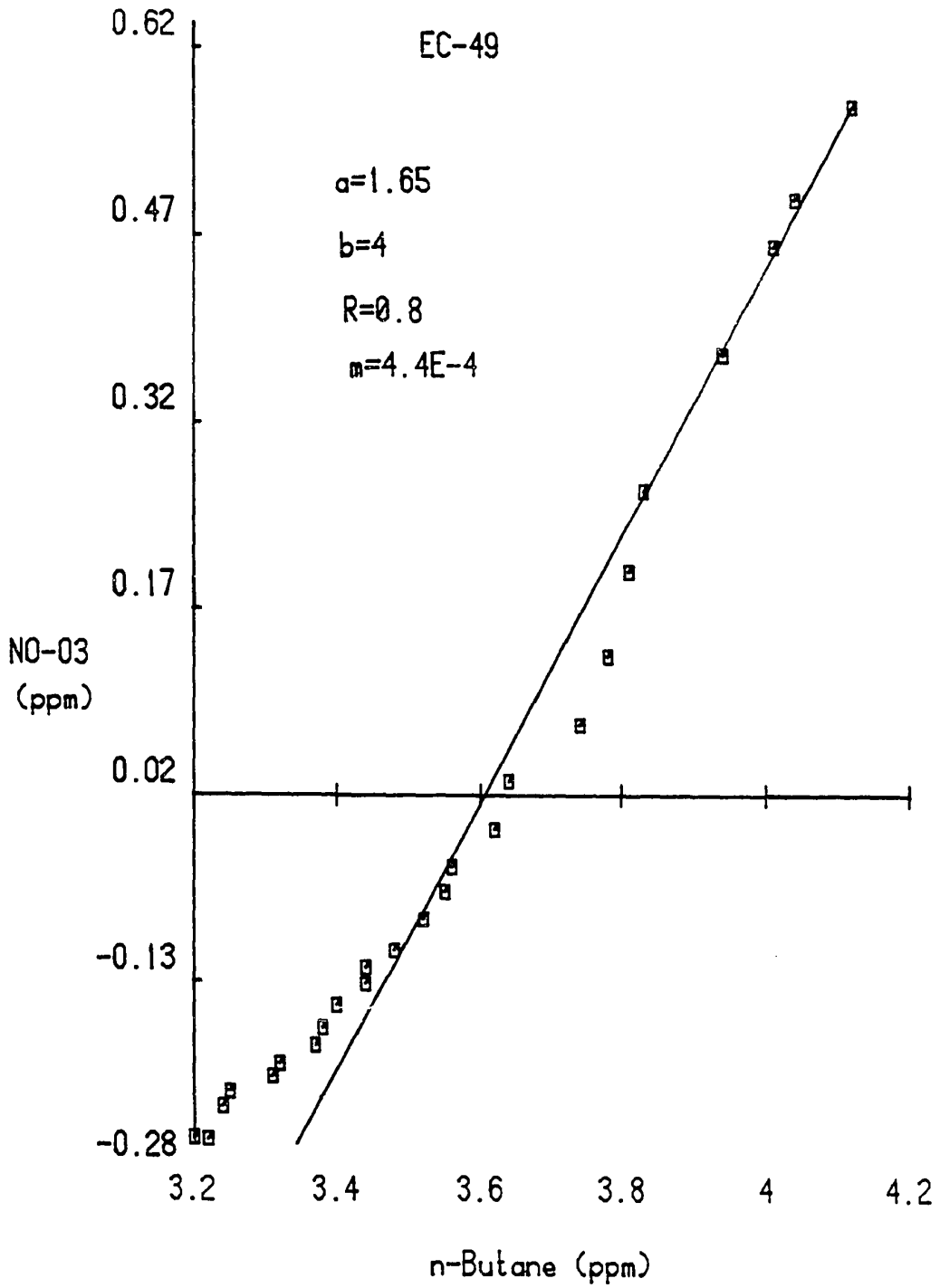


Figure 16. Simplified model prediction for EC-49.

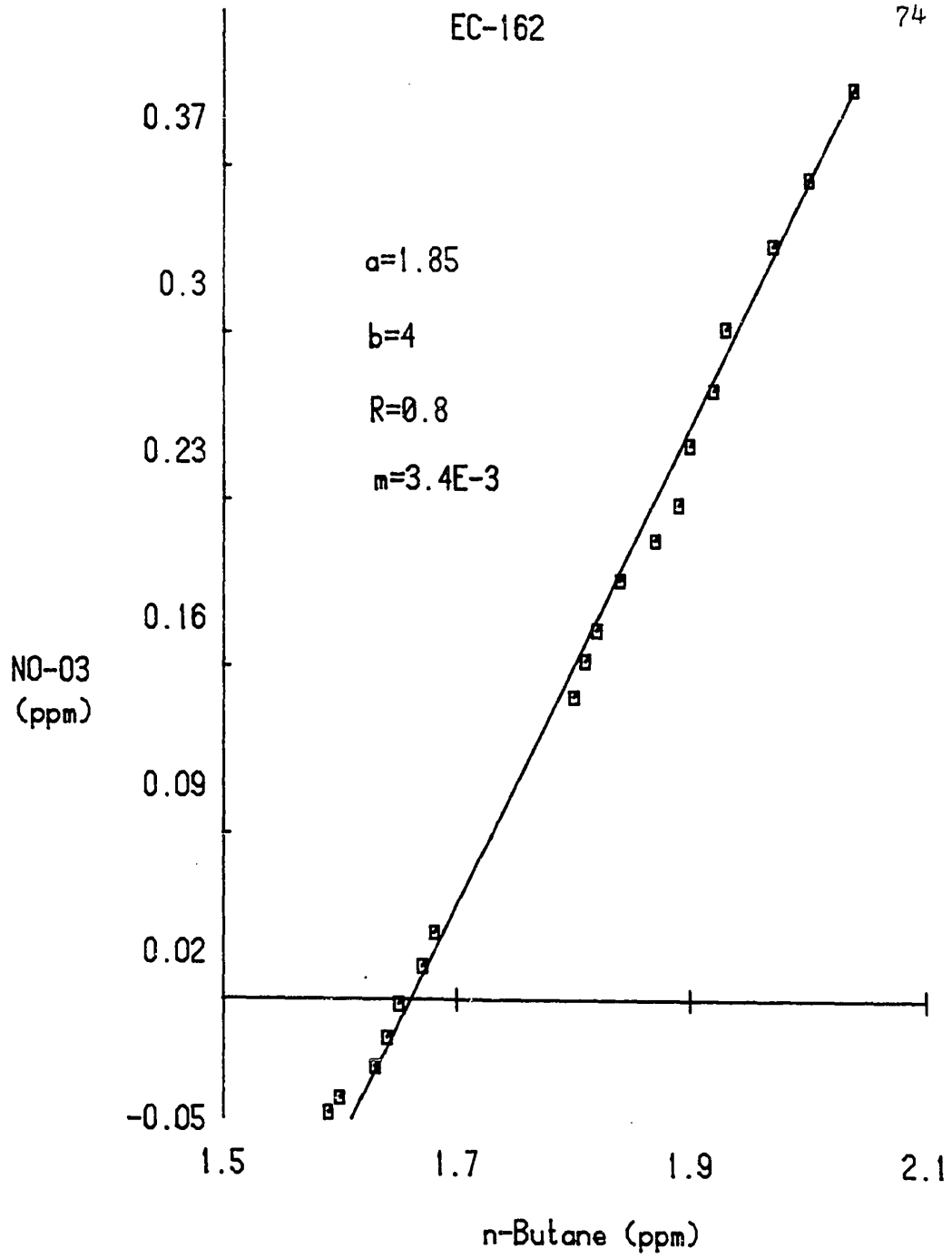


Figure 17. Simplified model prediction for EC-162.

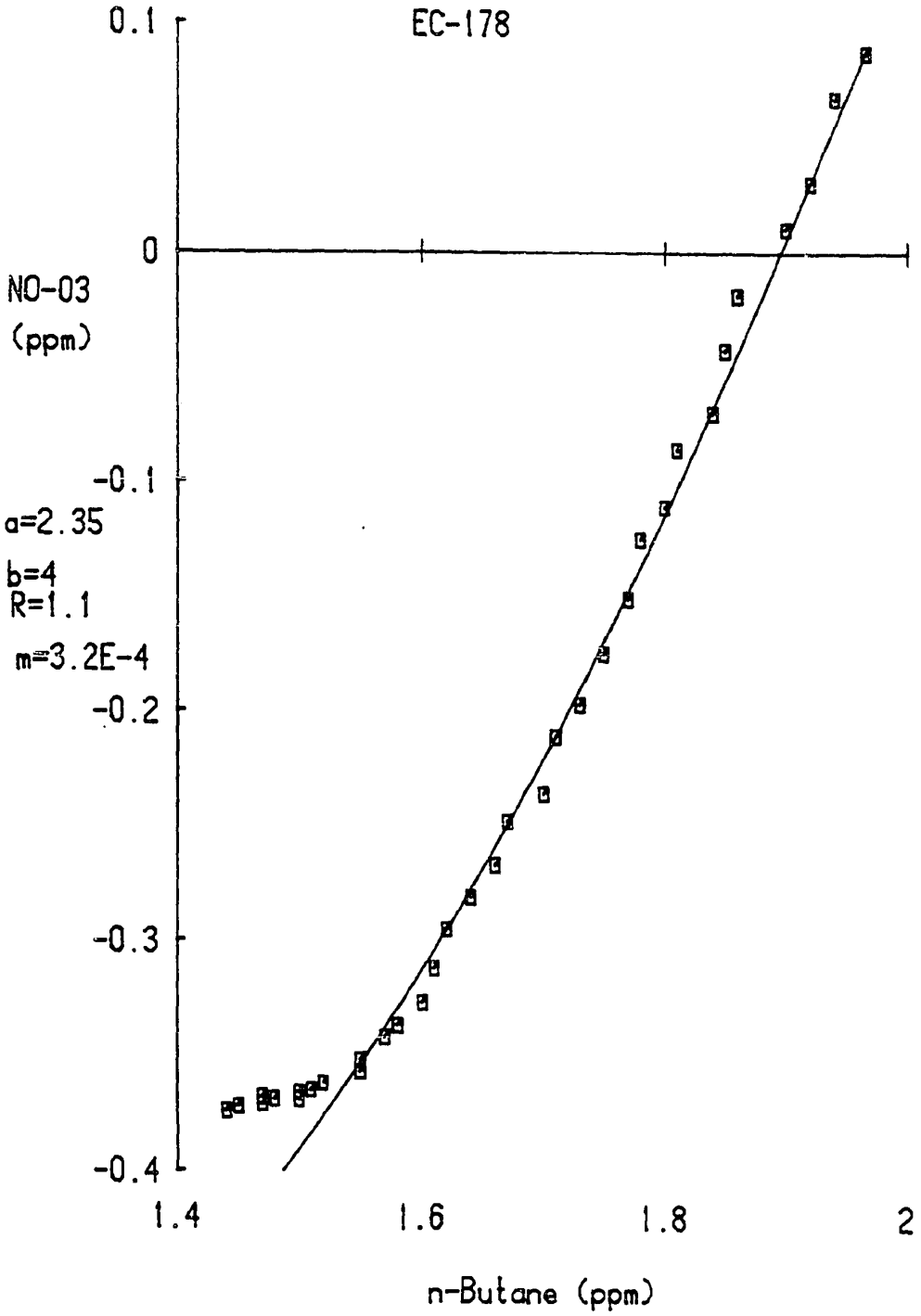


Figure 18. Simplified model prediction for EC-178.

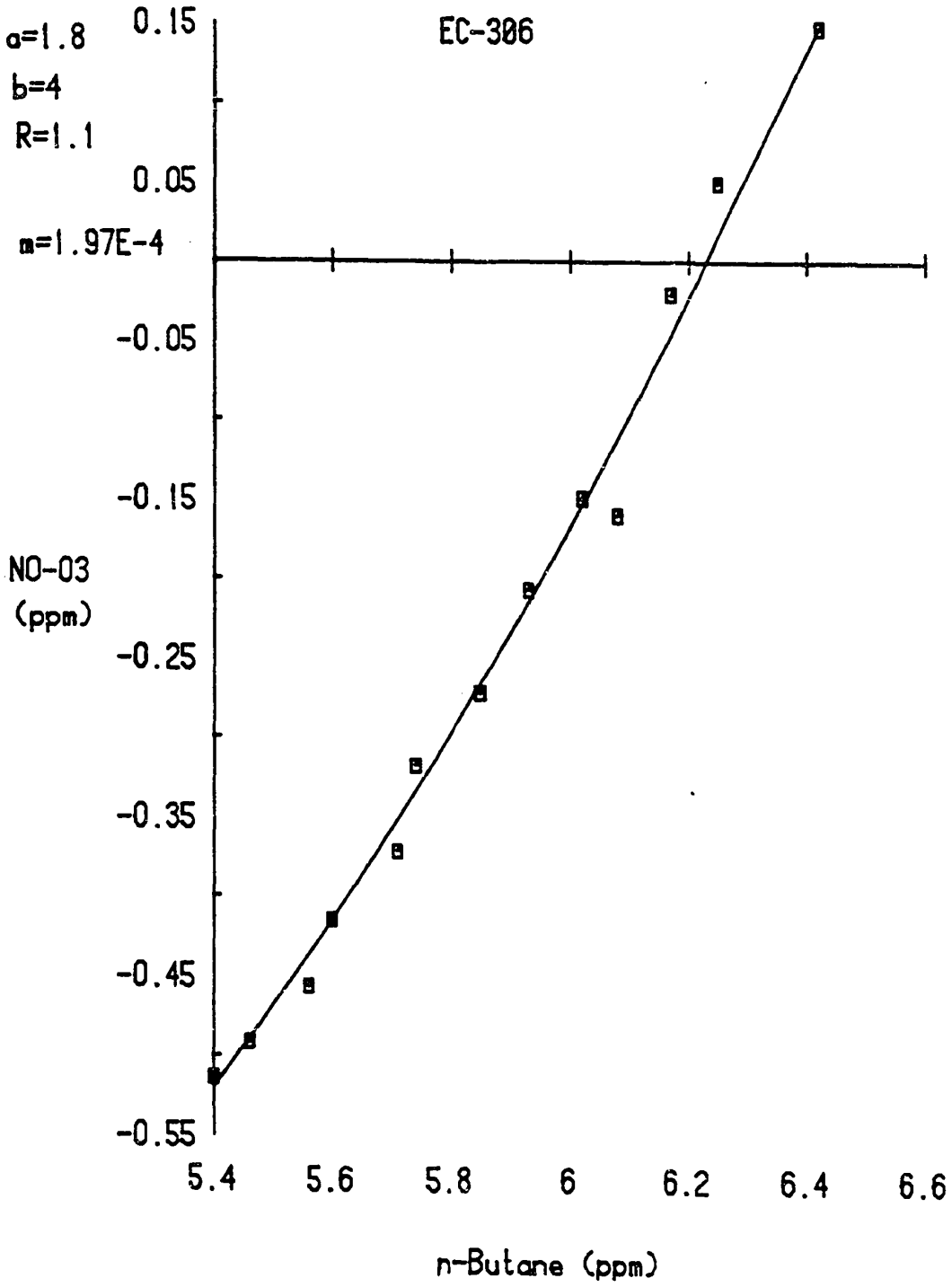


Figure 19. Simplified model prediction for EC-306.

also summarized in table (VI). The simplified NO-photooxidation model obtains the value for the coefficient "a" within ±%5 of the theoretical value (a=2), obtained by reference to the explicit mechanisms (42) and counting the number of NO --> NO2 conversions per destruction of hydrocarbon. The predicted value for "b" and R were 4 and 0.99±0.13 which correspond to methylethyl ketone which is the major product of n-Butane/NOx photooxidation (46,60).

The sensitivity of the model toward the variation of "R" can be observed in Fig (20). Notice that the simplified model is not very sensitive to this experimentally observed range of variation. This observation intutively is correct, since n-Butane is not a reactive hydrocarbon and as a consequence the concentration of the product of the n-Butane/NOx system does not reach to appreciable concentration.

It was observed that in some experiments e.g. EC-178 the model overpredicts the ozone concentration late in the ozone accumulation region. This overprediction is attributed to the lack of provision for the reactions that act as a sink for the removal of ozone. The most important removal paths for ozone include reactions such as ozone photolysis, reaction of ozone with NO2, and ozone wall loss. These reactions were left out from the NO photooxidation model simply because the contribution of these reactions in the NO-photooxidation regime are very small. But once NO is

TABLE VI

SUMMARY OF THE MODEL VALIDATION RESULTS FOR
n-butane/NO_x

EC-no.	[HC] ppm	[NO] ppm	m/k*	m (min)	a	b	R
304	4.28	0.349	0.9	2.4E-4	1.9	4	1.1
309	4.31	0.203	1.2	3.2E-4	1.75	4	1.1
39	4.03	0.524	1.13	3.9E-4	2	4	0.95
47	3.90	0.534	1.42	3.4E-4	1.8	4	1.1
308	4.05	0.305	0.46	4.4E-4	1.6	4	0.9
49	4.12	0.553	1.81	4.4E-4	1.65	4	0.8
162	2.049	0.382	1.13	3.4E-3	1.85	4	0.8
178	1.96	0.087	1.05	3.2E-4	2.35	4	1.1
306	6.44	0.147	0.74	2.0E-4	1.8	4	1.1

*m/k represents the relative reactivity of n-butane with respect to the rate of dilution (k).

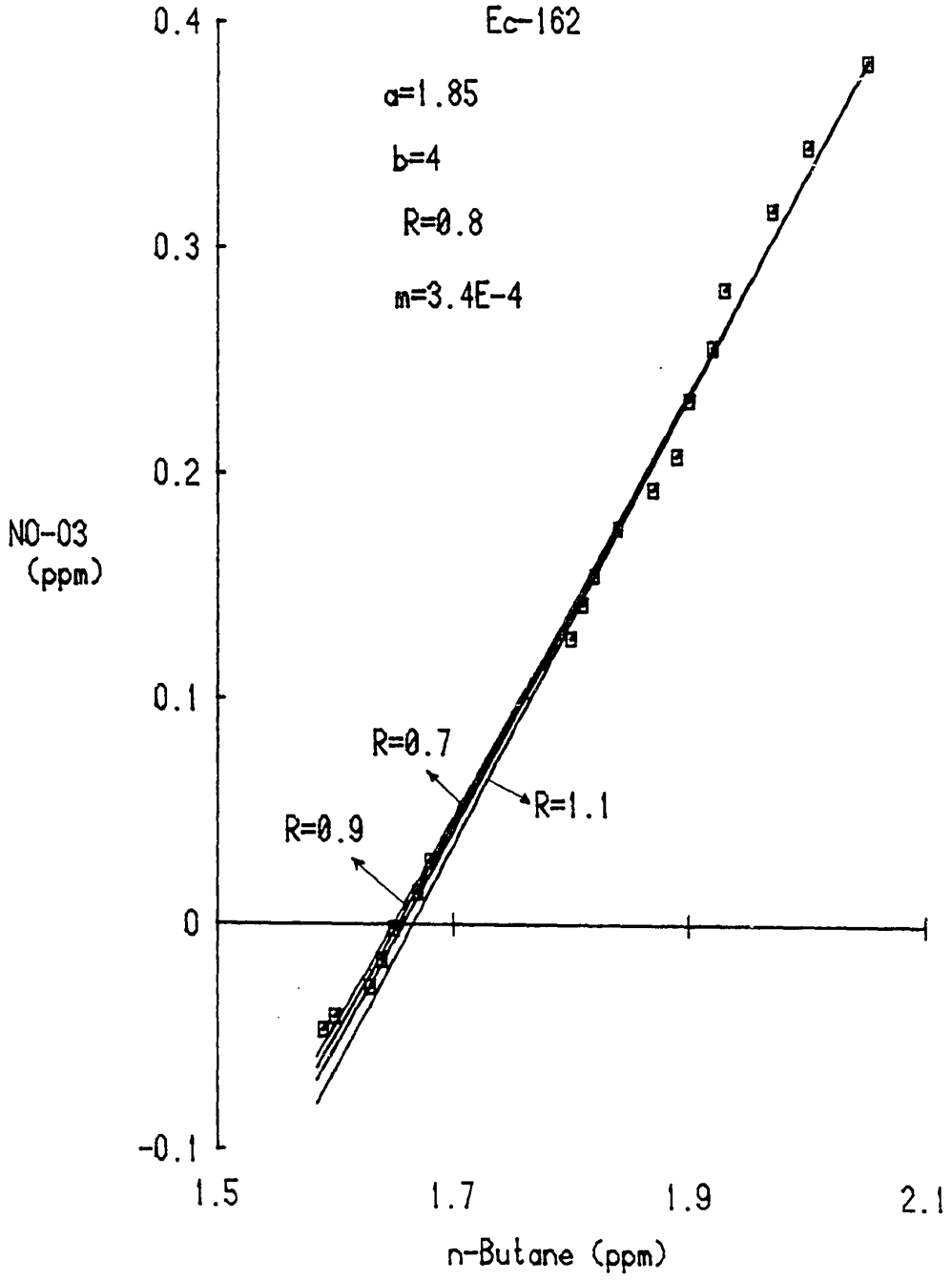


Figure 20. Model's sensitivity with variation in "R".

depleted, i.e., NO2 and ozone reach appreciable concentration these removal paths become significant and their contribution for an accurate prediction of ozone concentration must be considered. These ozone removal paths are discussed in chapter VII.

VI-c Effect of Dilution for n-Butane/NOx

In order to investigate the effect of dilution on predicted results for n-Butane/NOx, the dilution rate was varied. Results of such experiments are presented in Figure (21). In this figure "k" is the reported value for the rate of dilution (76). Notice that the model's prediction are very sensitive to the value of k. If the dilution rate varies by a factor of two a pronounced change in the outcome results. This conclusion requires that for an accurate assessment of the ozone forming potential of an unreactive hydrocarbon, dilution must be considered and ignoring this term is a major oversight.

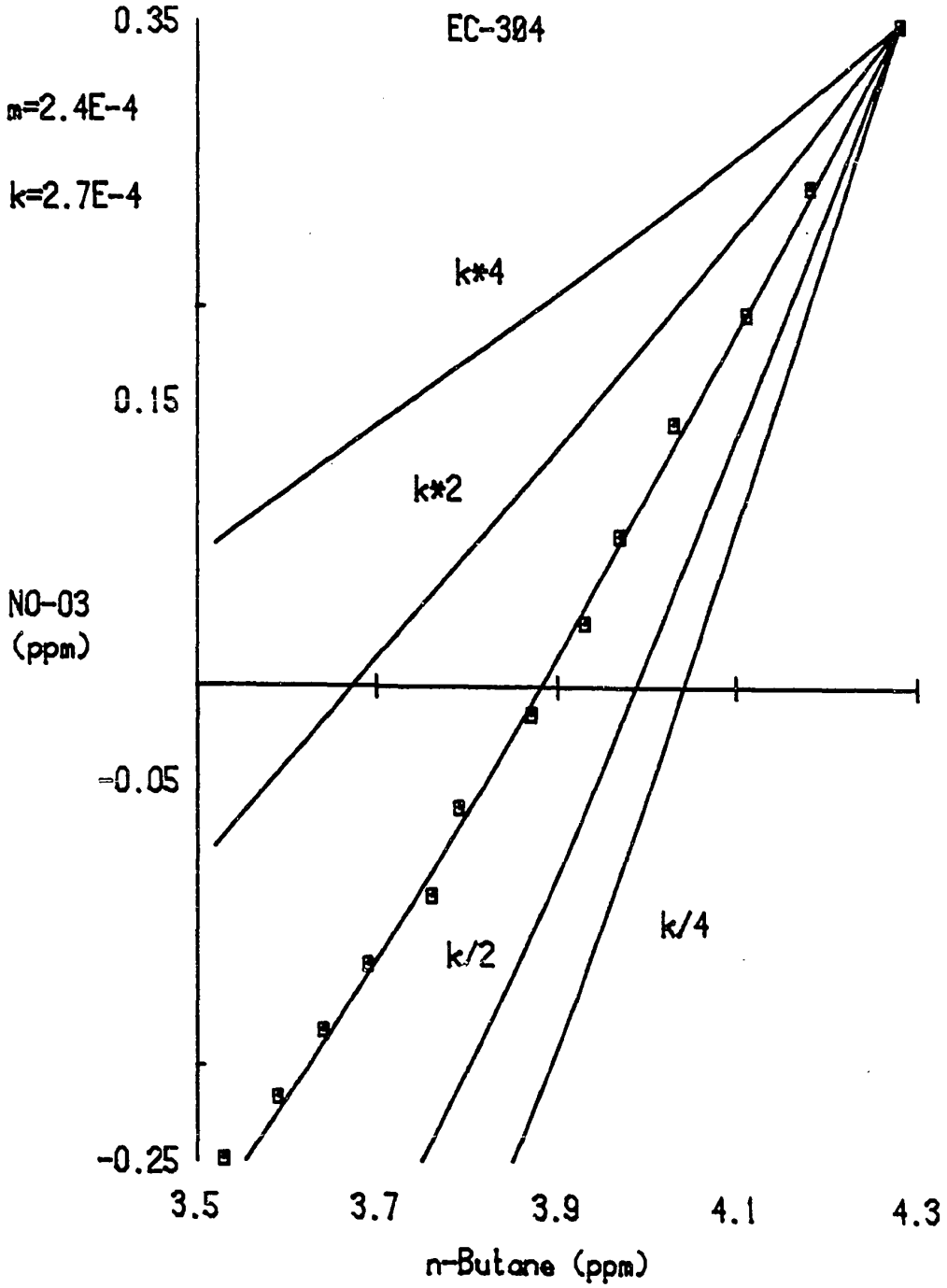


Figure 21. Model's sensitivity with the rate of dilution for n-Butane/NO_x system.

VI-d Application of model to Propene/NOx smog chamber data

Propene is the second hydrocarbon to which the model is applied. Due to the reaction of propene with ozone we first applied the model at low HC/NO ratios where the inhibitory effect of nitric oxide retards ozone buildup. Also, this low ratio corresponds more closely with the assumptions used in the NO-photooxidation model. In figure (22) we plot [NO-O3] vs. [Propene] for UCR smog chamber experiment EC-256. The best fit to this experiment was obtained with values of 2.35, 4, 0.5 for a,b and R respectively. The hydrocarbon reactivity for this experiment is presented in figure (23). Notice the constant slope of such a plot is again in good agreement with our assumption of constant hydroxyl radical concentration. (For unsaturated aliphatic hydrocarbons which make up about 10-15% of the observed total hydrocarbon in the real atmosphere this constant slope does not occur due to the rection of ozone and OH with the hydrocarbon). More examples of low HC/NO ratio experiments are presented in figures (24-30). These include data from UCR as well as our own experimental data. The predicted values for the empirical parameters a, b and R for UCR and our smog chamber are in good agreement with the theoretical values reported (42). The theoretical values for the coefficients a, b and R are 2, 4 and 0.5 which correspond to acetaldehyde and formaldehyde as the major products of this system (42). The

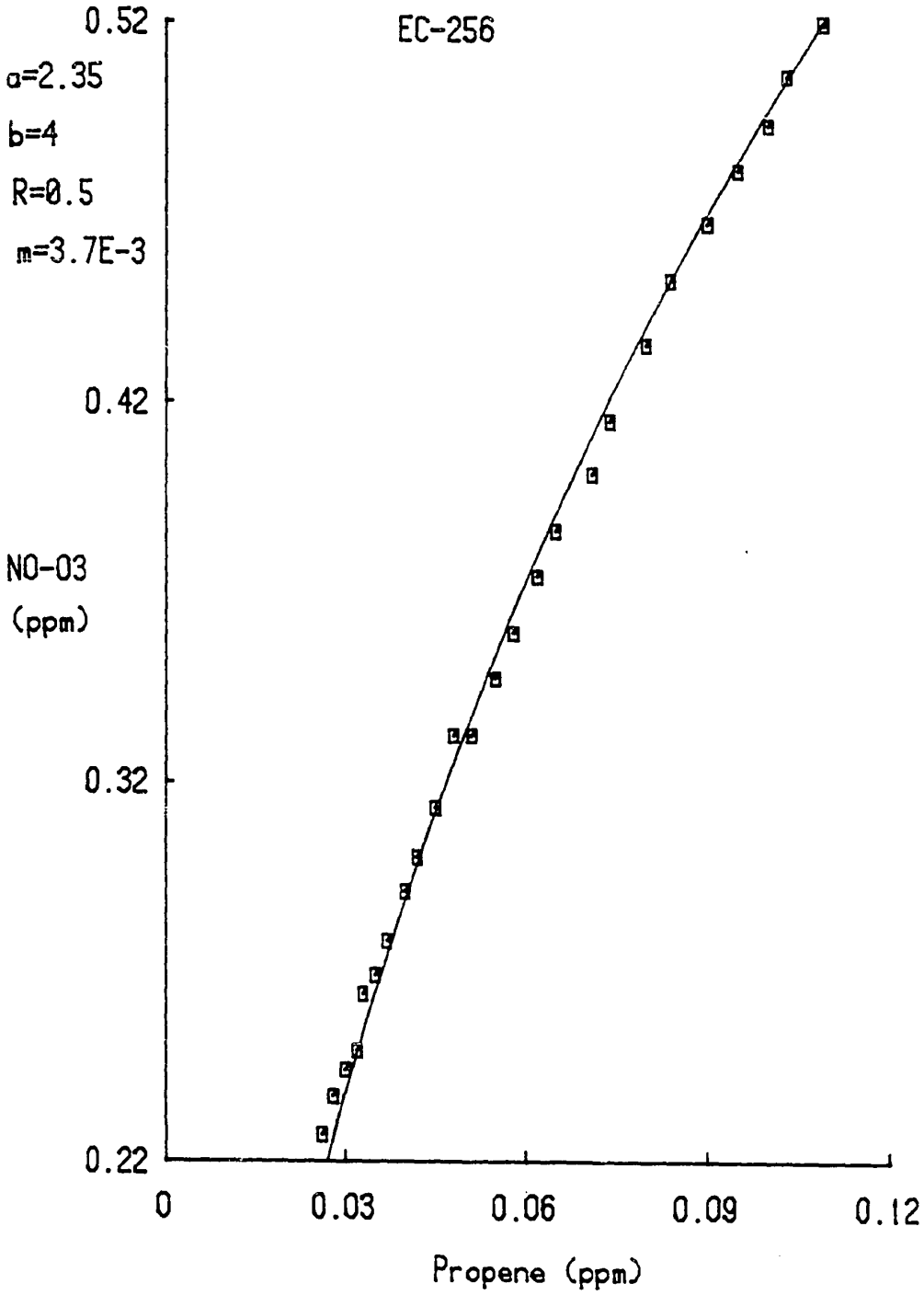


Figure 22. Simplified model prediction for EC-256.

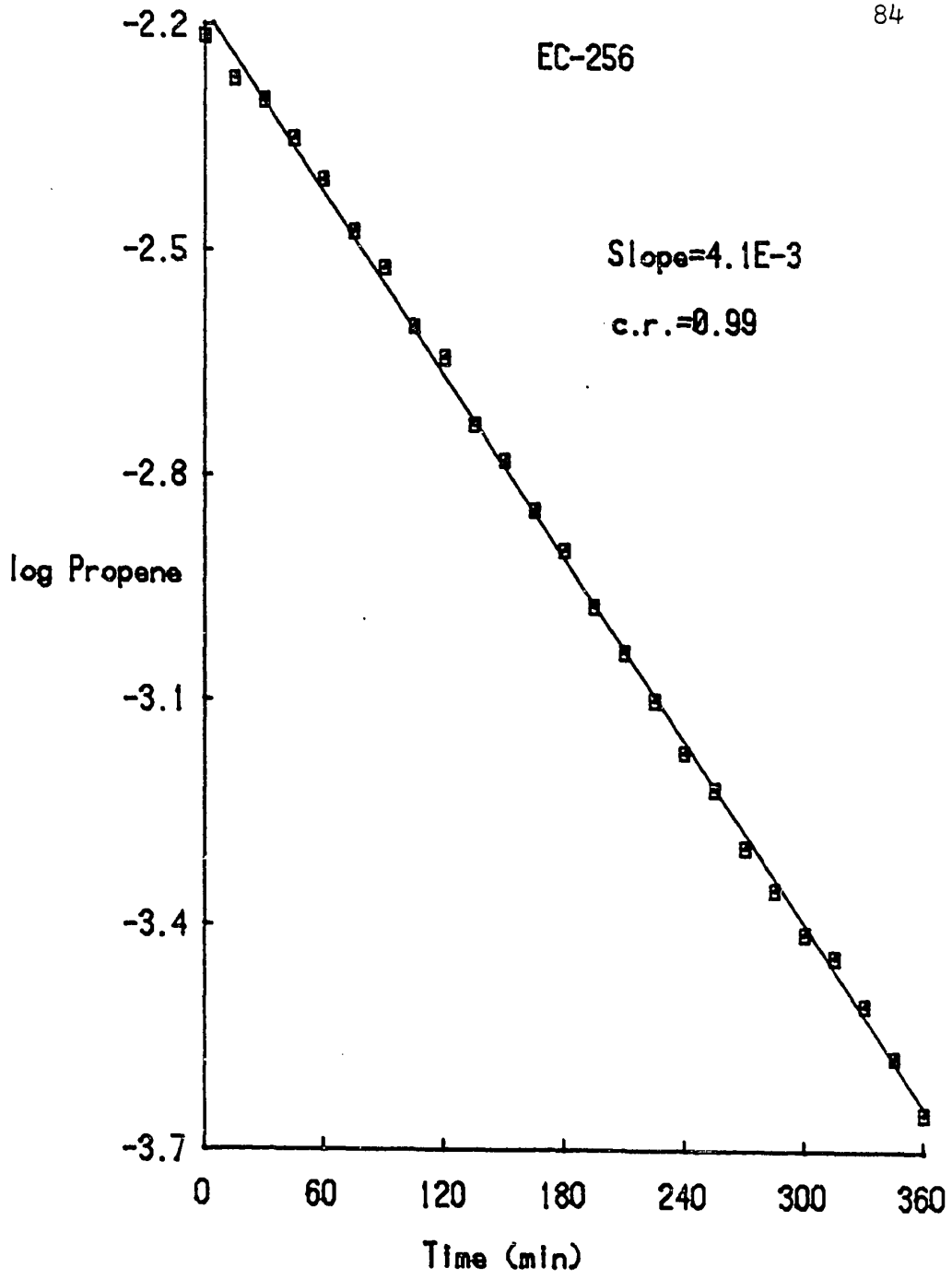


Figure 23. Hydrocarbon's reactivity for propene EC-256.

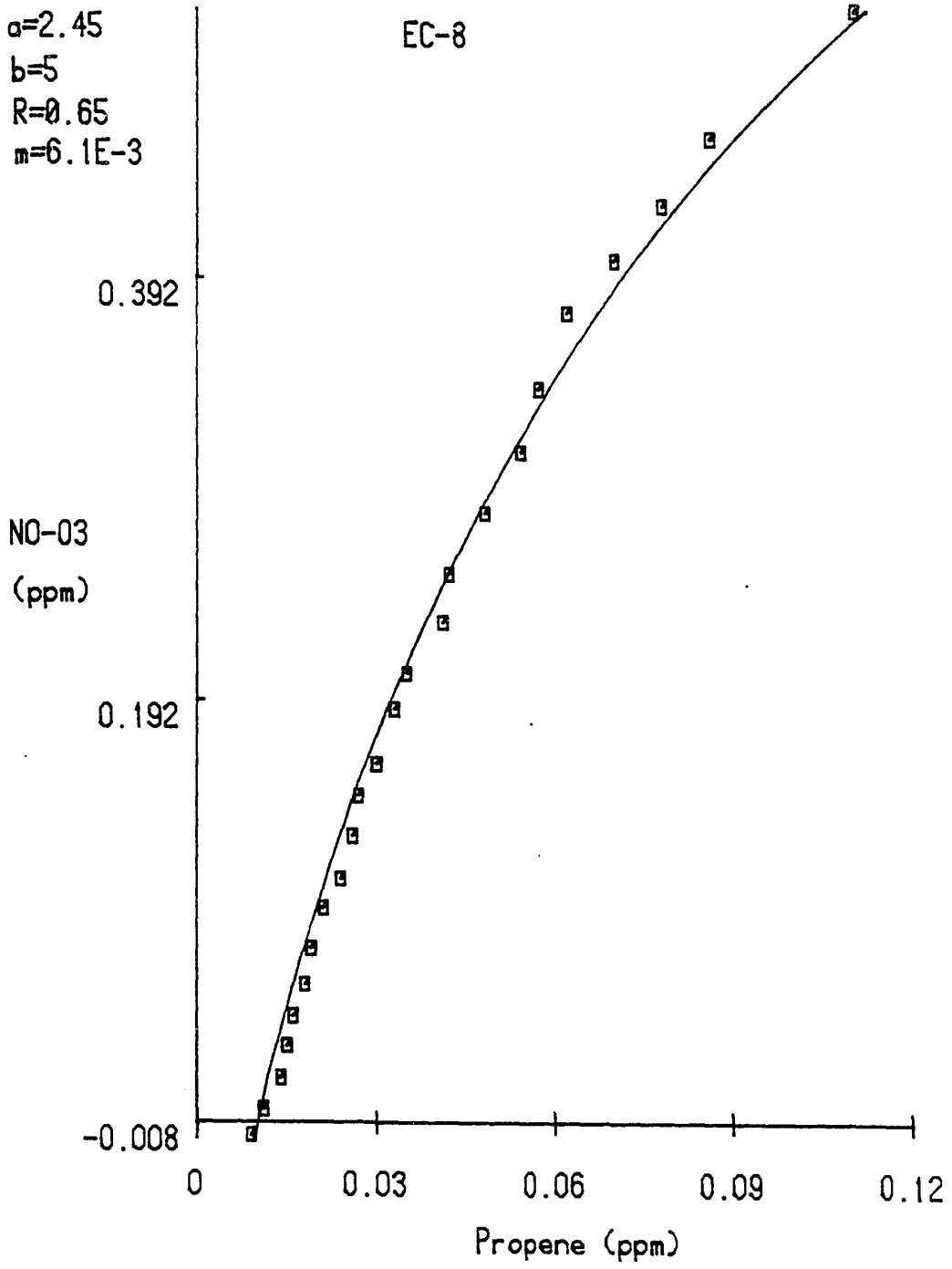


Figure 24. Simplified model prediction for EC-8.

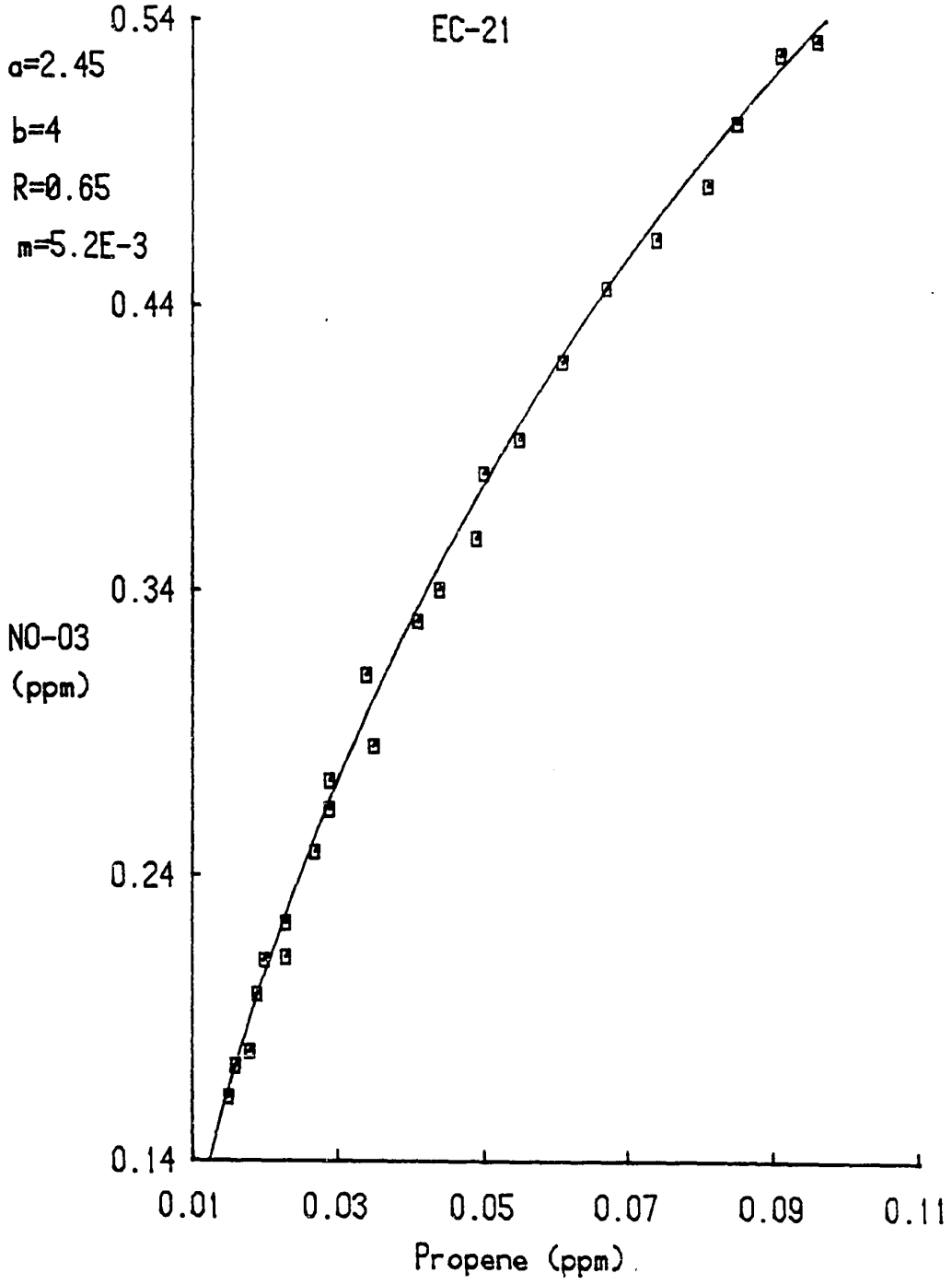


Figure 25. Simplified model prediction for EC-21.

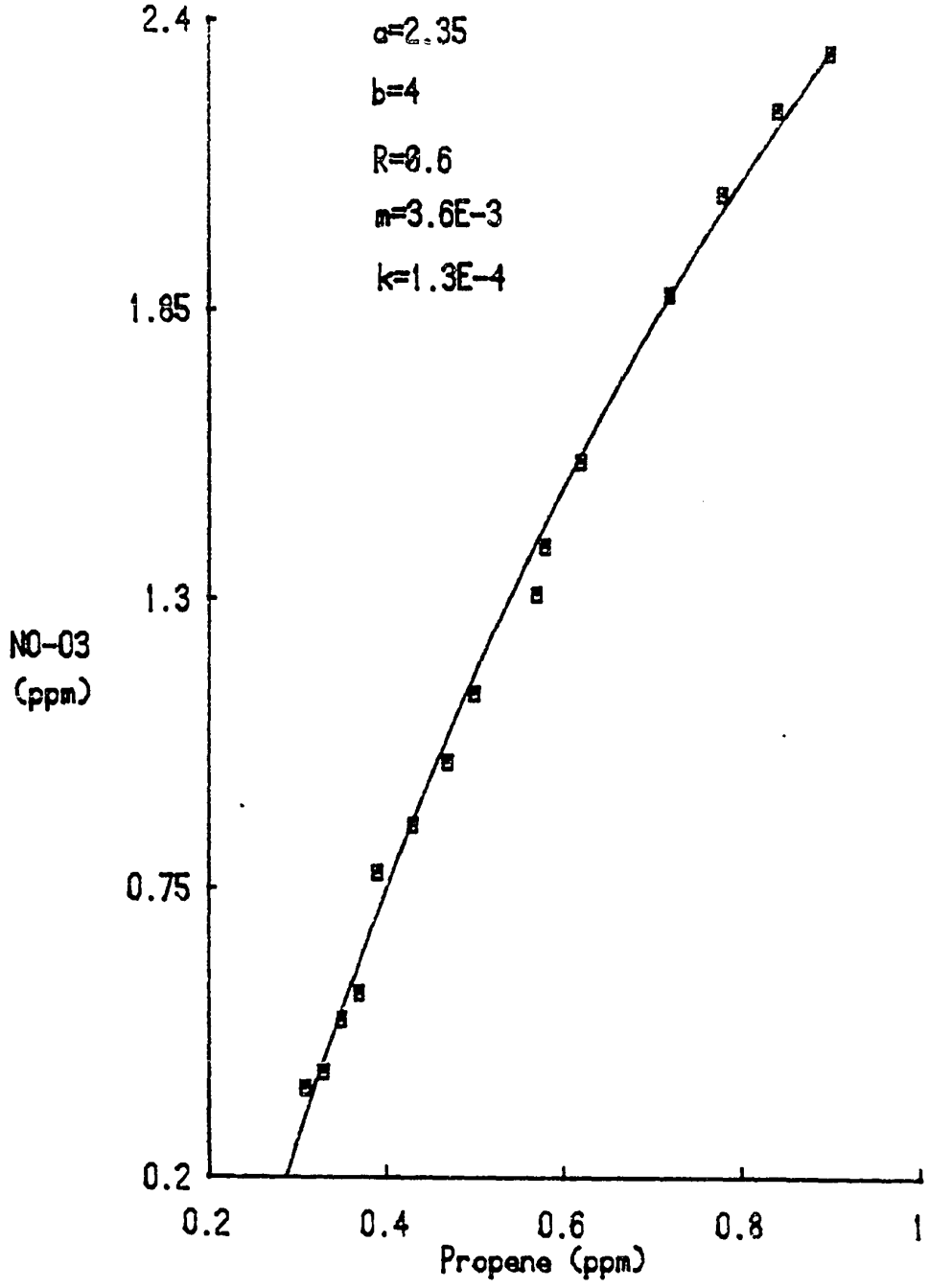


Figure 26. Simplified model prediction for our data.

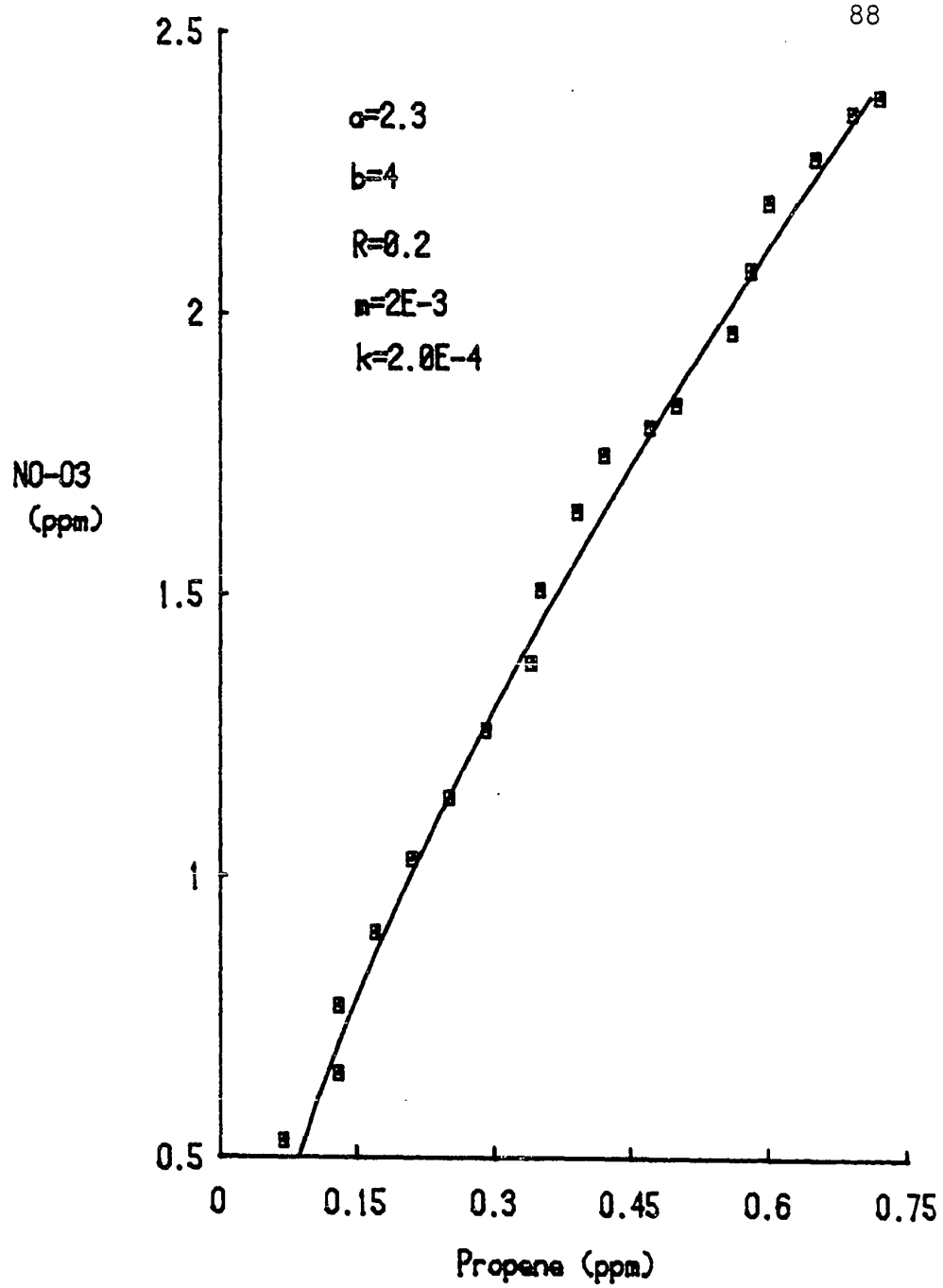


Figure 27. Simplified model prediction for our data.

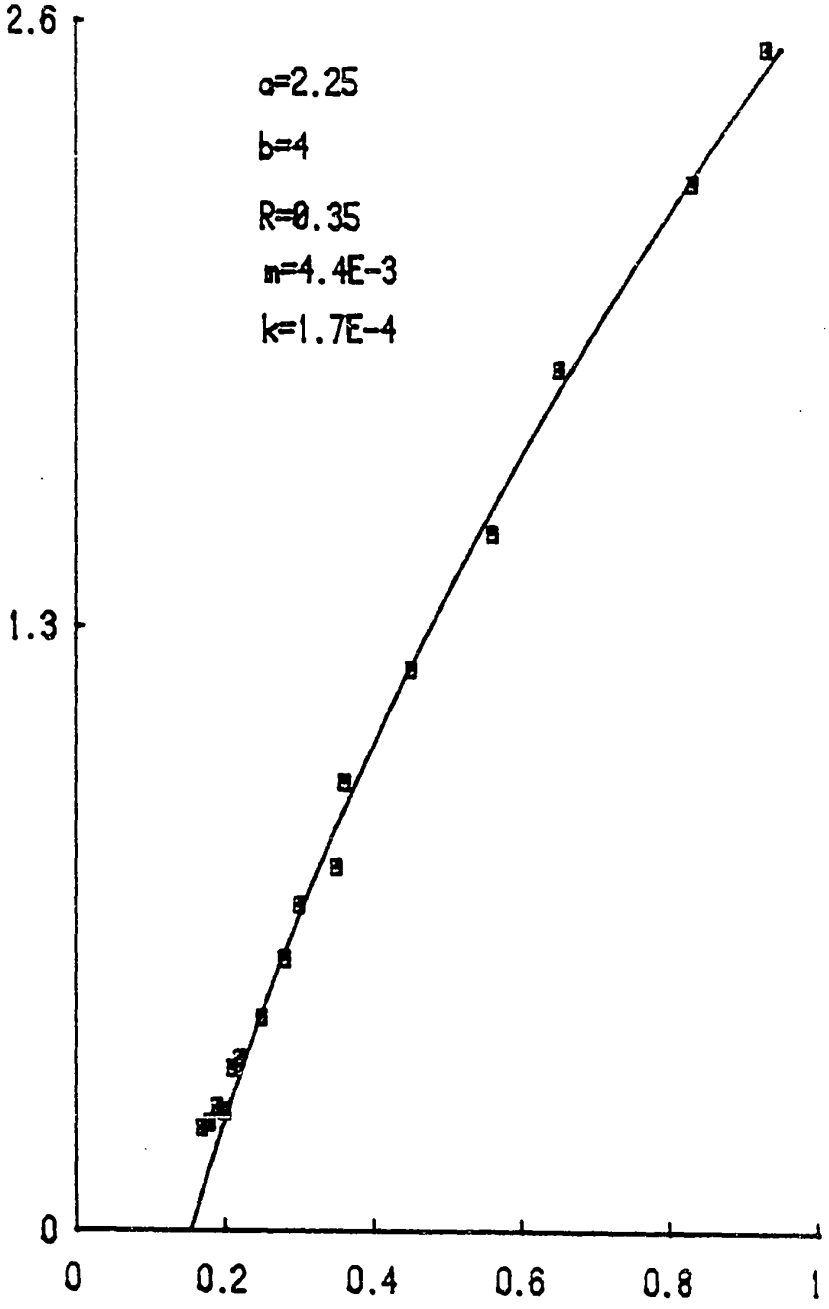


Figure 28. Simplified model prediction for our data.

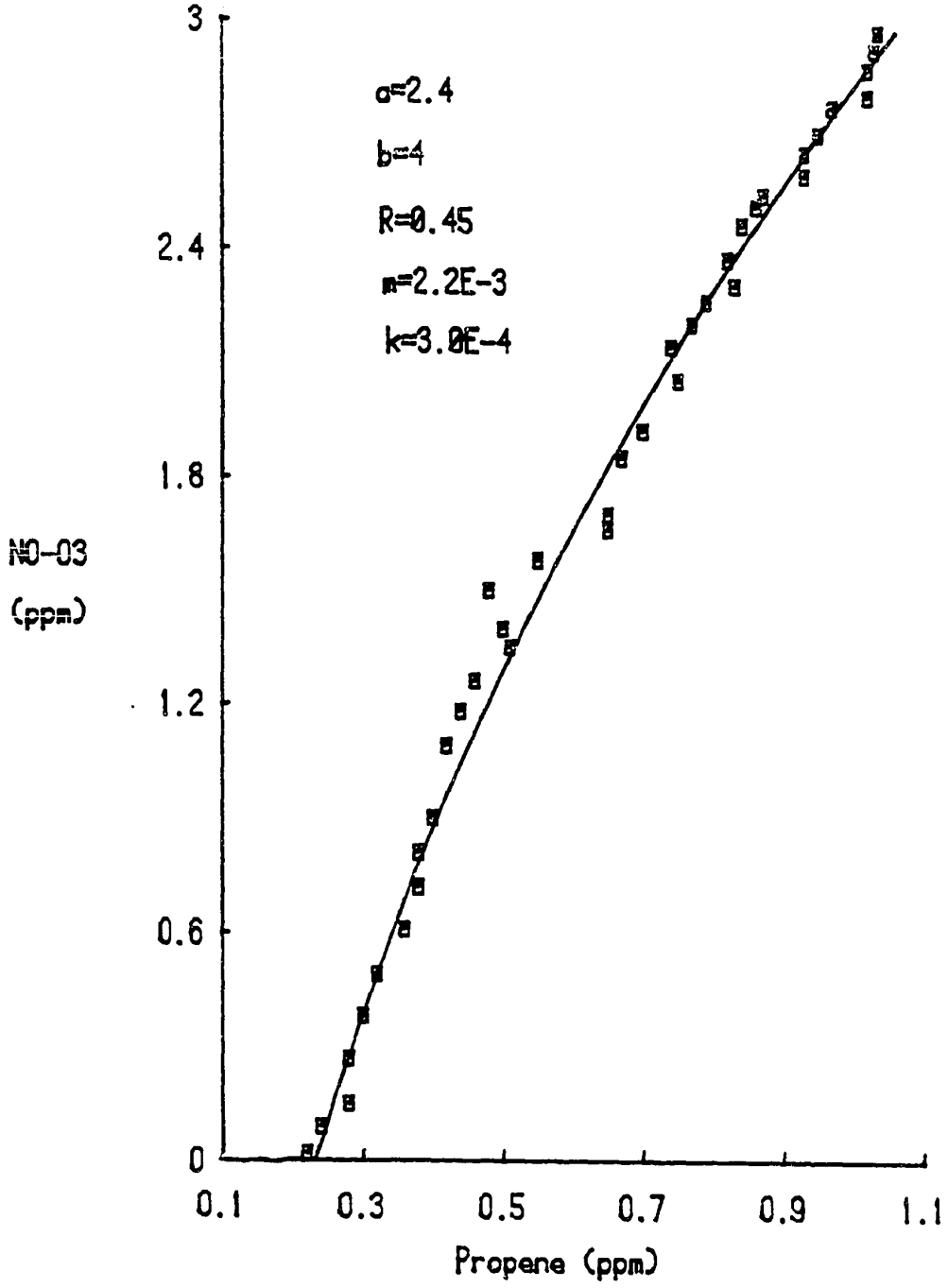


Figure 29. Simplified model prediction for our data.

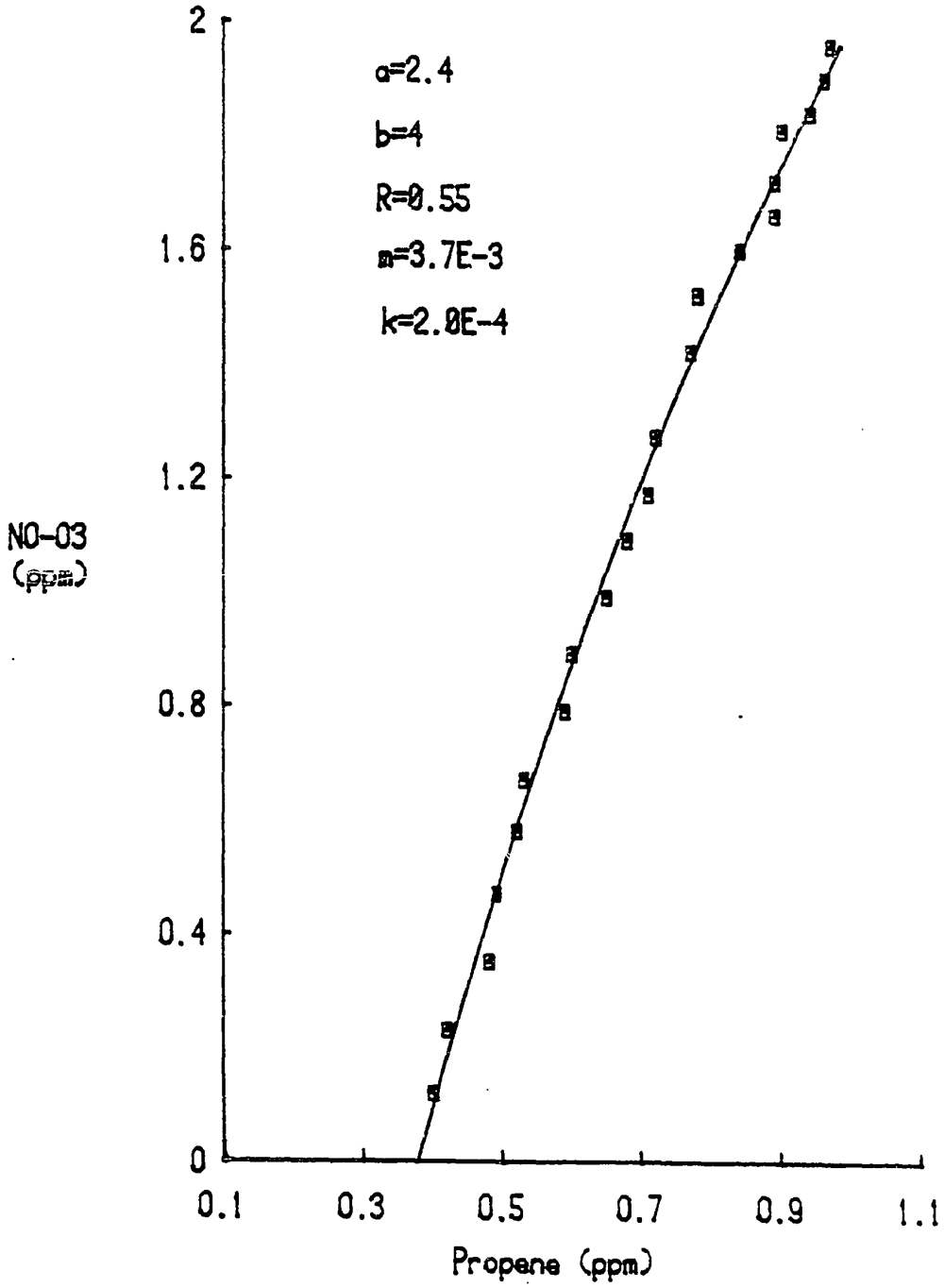


Figure 30. Simplified model prediction for our data.

value of "a" represents the number of NO-->NO2 conversions for removal of propene by hydroxyl radical. The value for "b" is the total number of NO-->NO2 conversions for removal of acetaldehyde (b=3) and formaldehyde (b=1) by OH, and "R" will represent the weighted average of the removal rate of formaldehyde and acetaldehyde with respect to propene by OH.

It was observed that as the HC/NO ratio increased, the NO photooxidation model overpredicted the ozone concentration in the later part of the experiments, i.e., the ozone accumulation region. An example is shown in figure (31) which corresponds to the ratio of 0.77. The model reasonably well reproduces the NO-photooxidation region and early ozone accumulation period, but it overpredicts the ozone concentration in late ozone accumulation region. It was also noticed that with increasing HC/NO ratios, the model started to overpredict the ozone concentration sooner. Some examples of these observations (in order of increasing HC/NO ratios) are presented in figures (32-35). In order to compensate for the ozone overprediction we had to use a very small value for R. An example of this case is presented in Fig. (36). Notice that even with such a small value for R the model still overpredicts the concentration of ozone in the ozone accumulation region. Therefore, at this stage we were confronted with two problems:

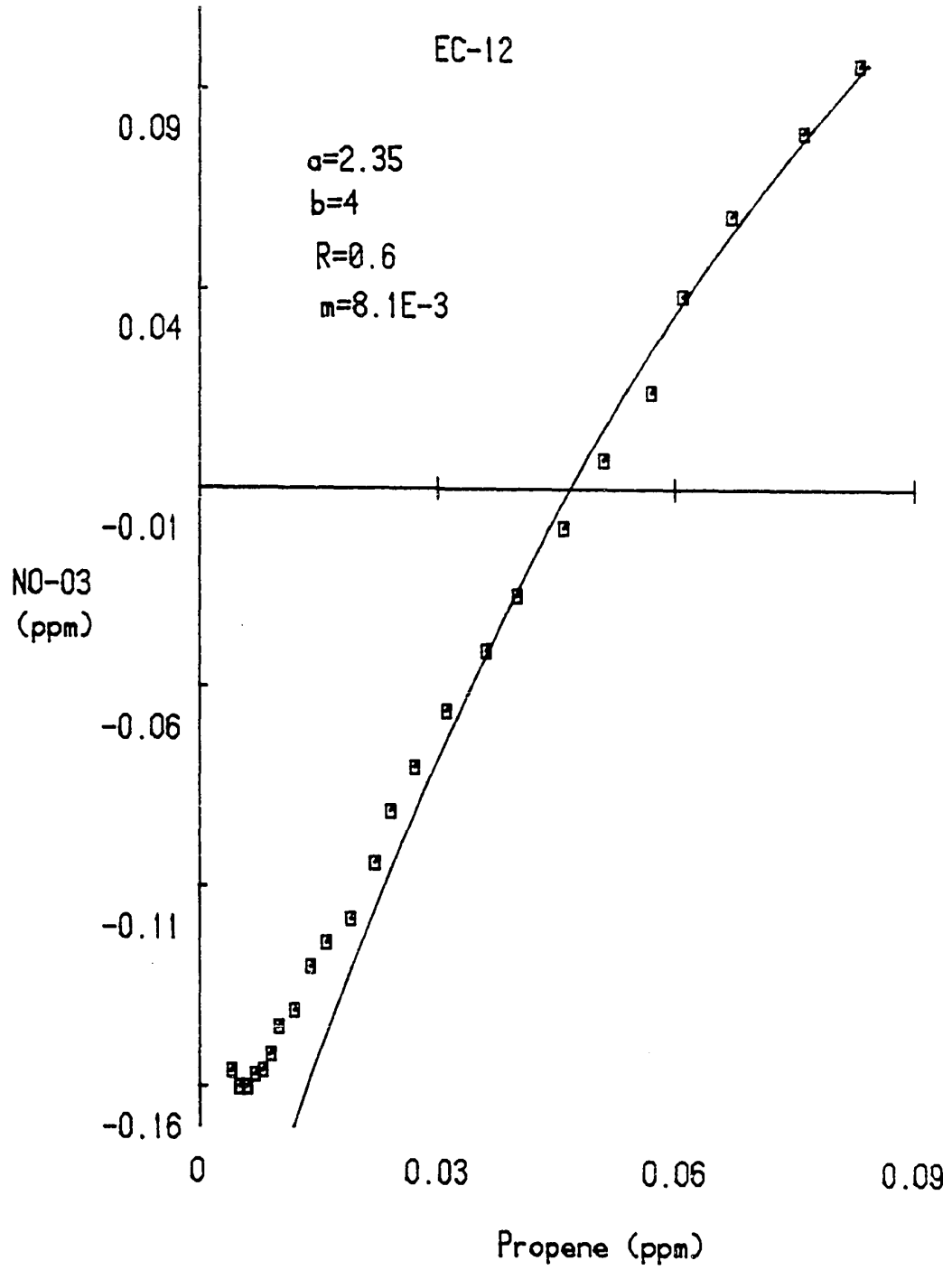


Figure 31. Simplified model prediction for EC-12.

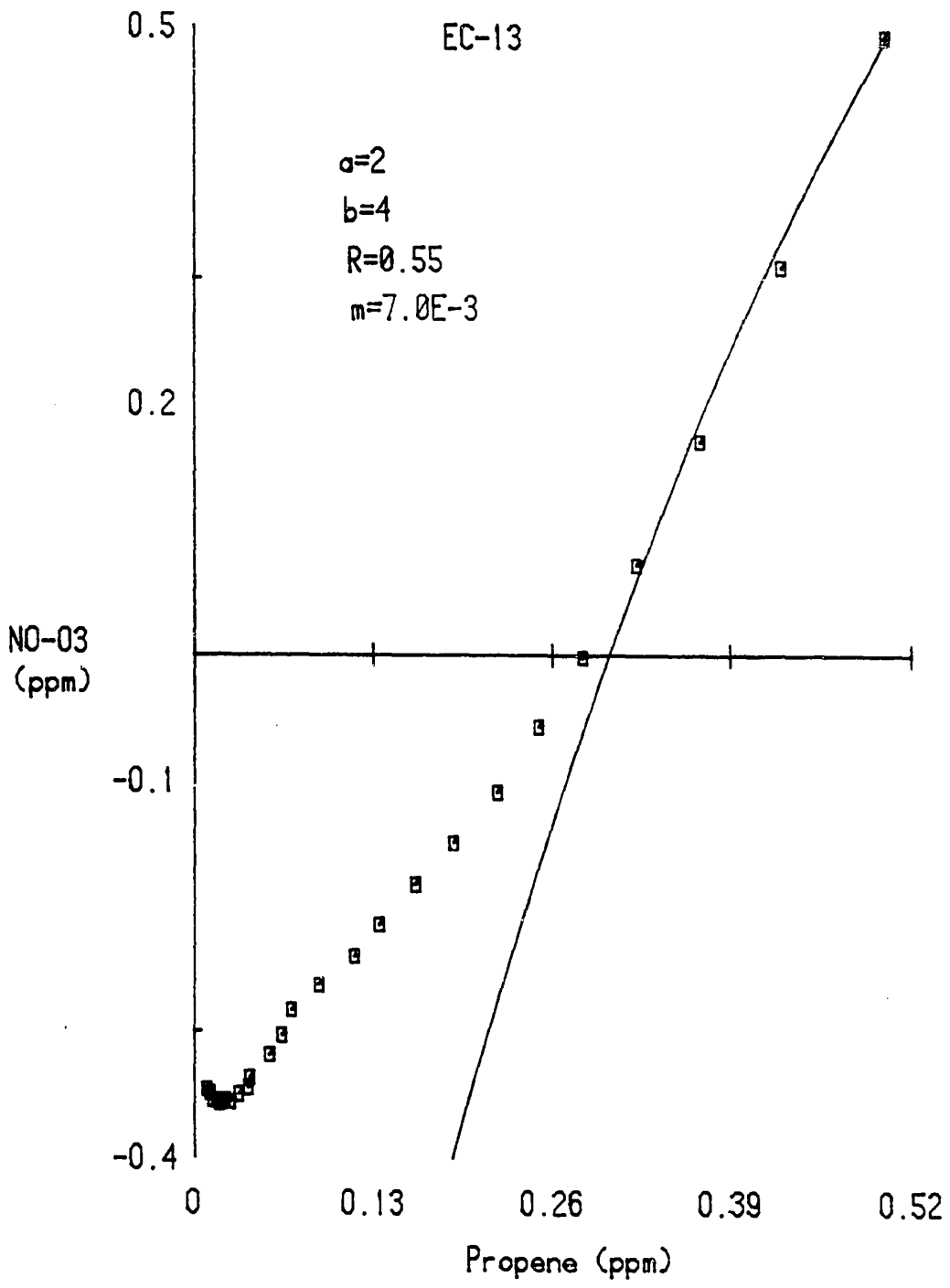


Figure 32. Simplified model prediction for EC-13.

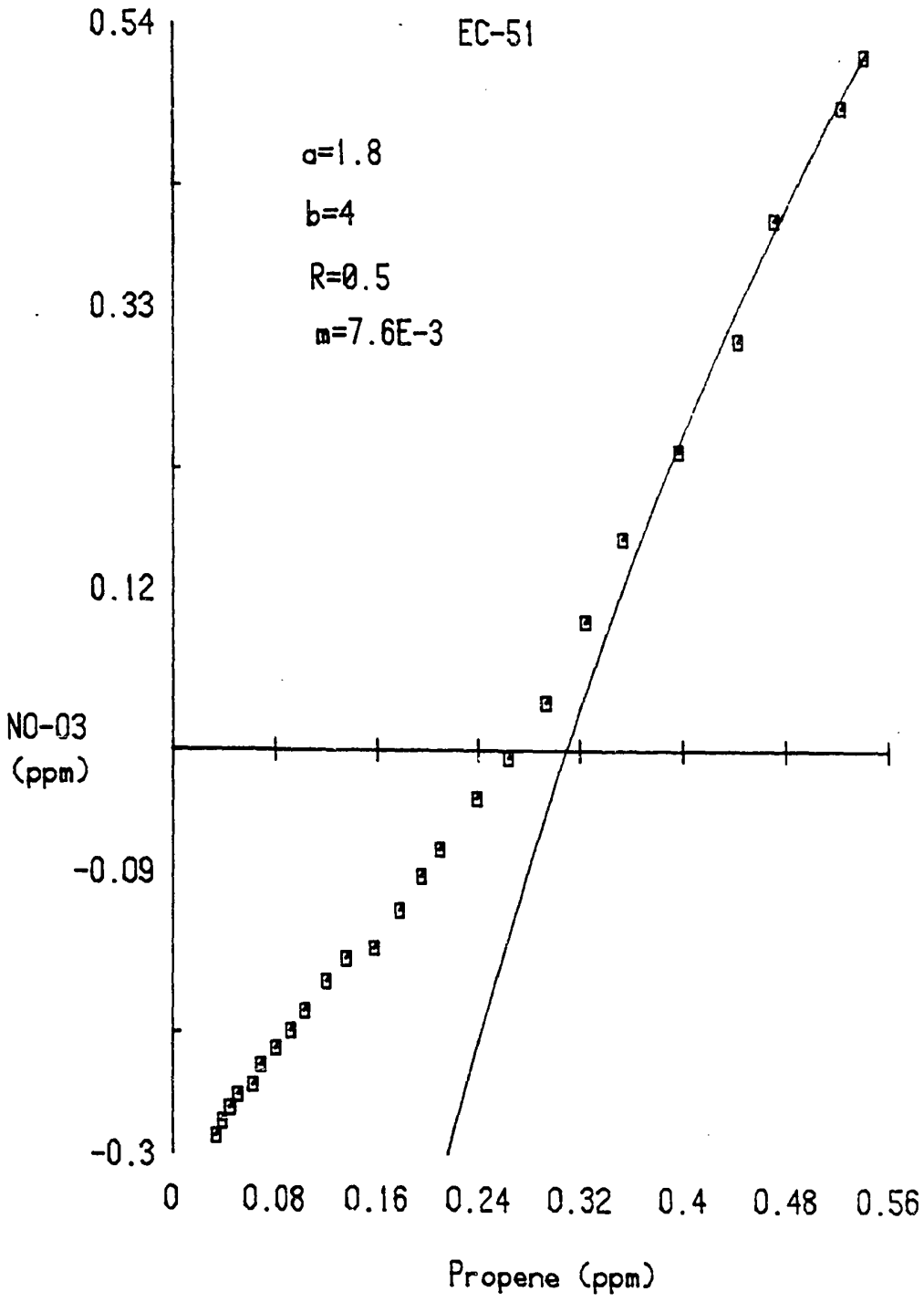


Figure 33. Simplified model prediction for EC-51.

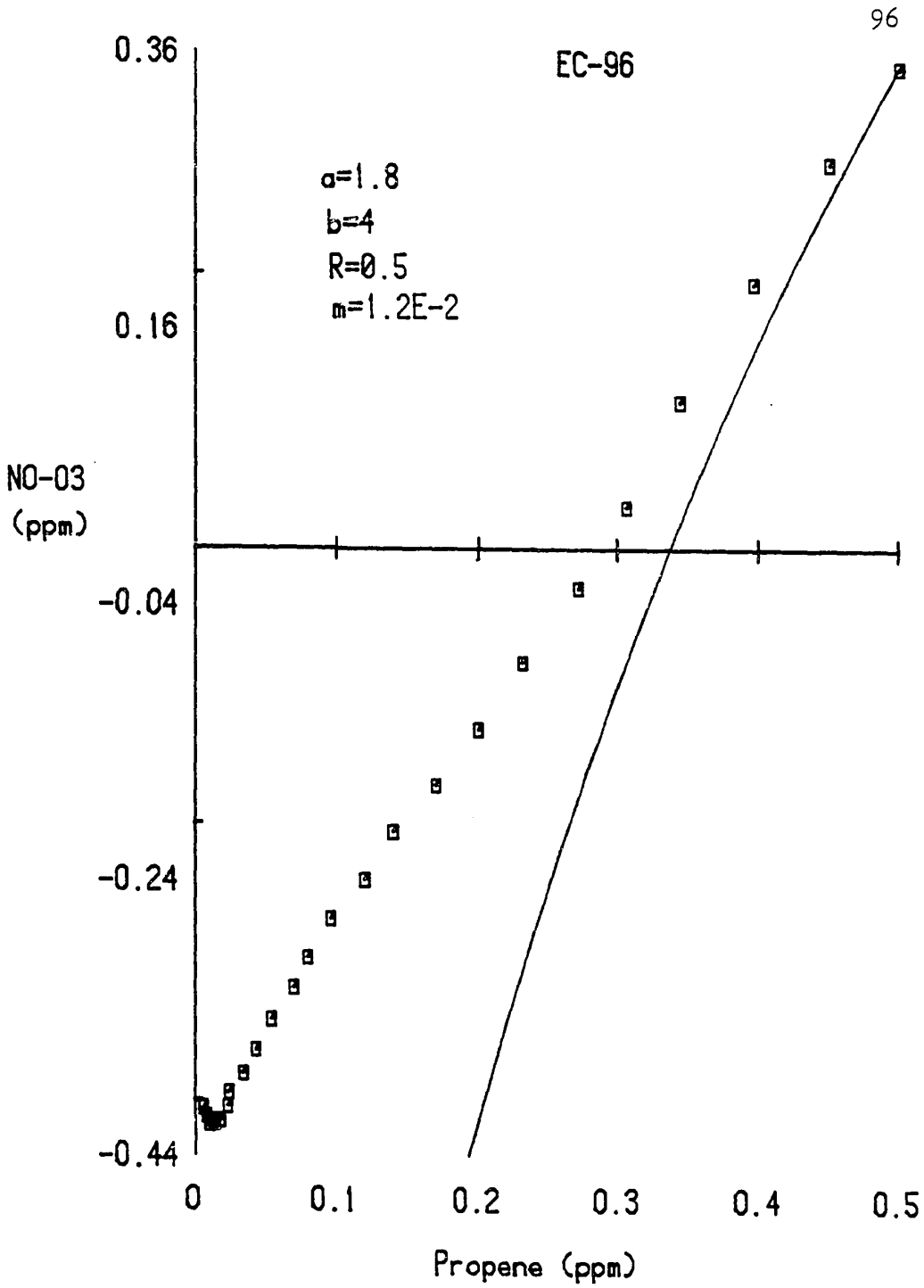


Figure 34. Simplified model prediction for EC-96.

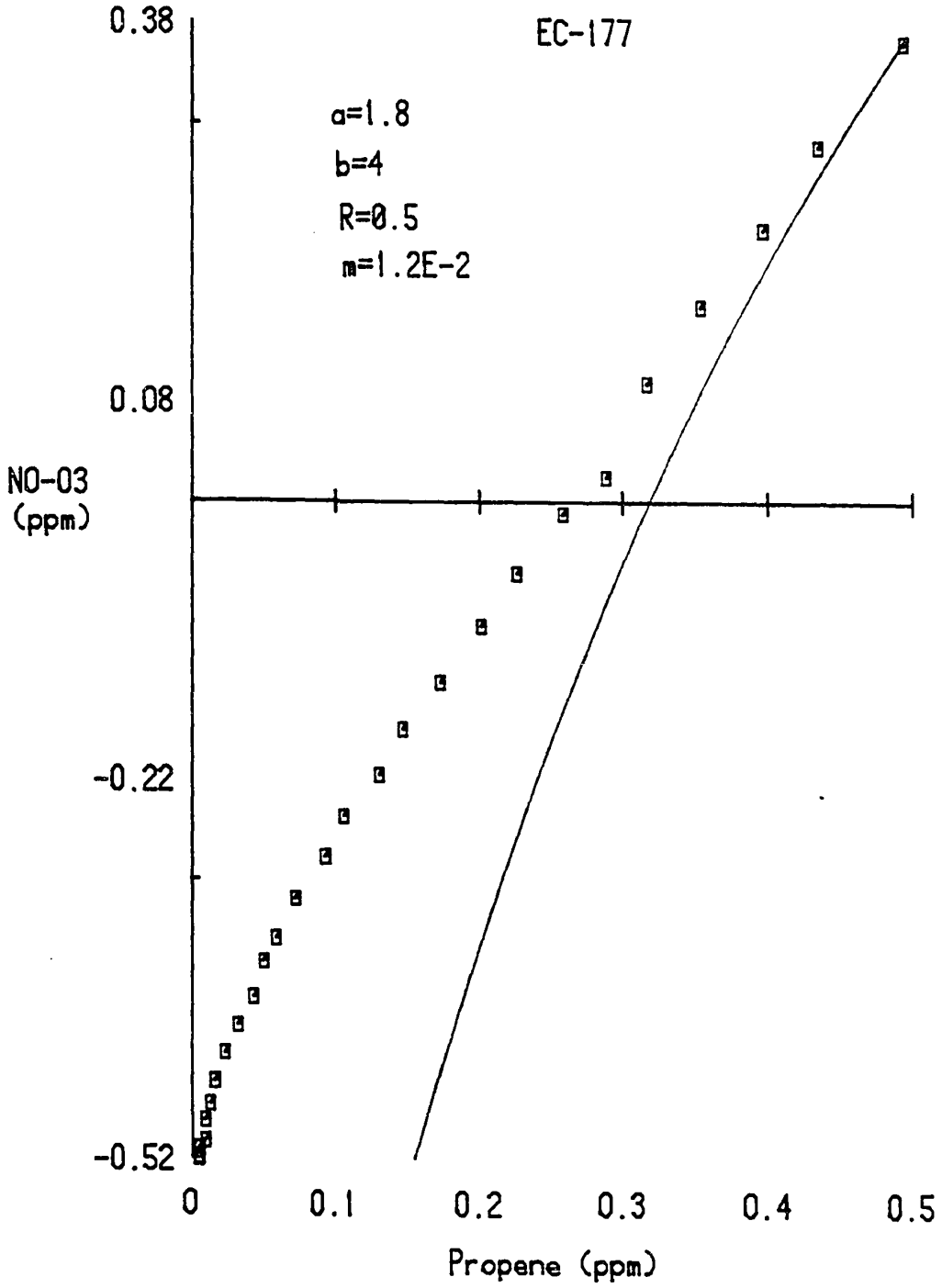


Figure 35. Simplified model prediction for EC-177.

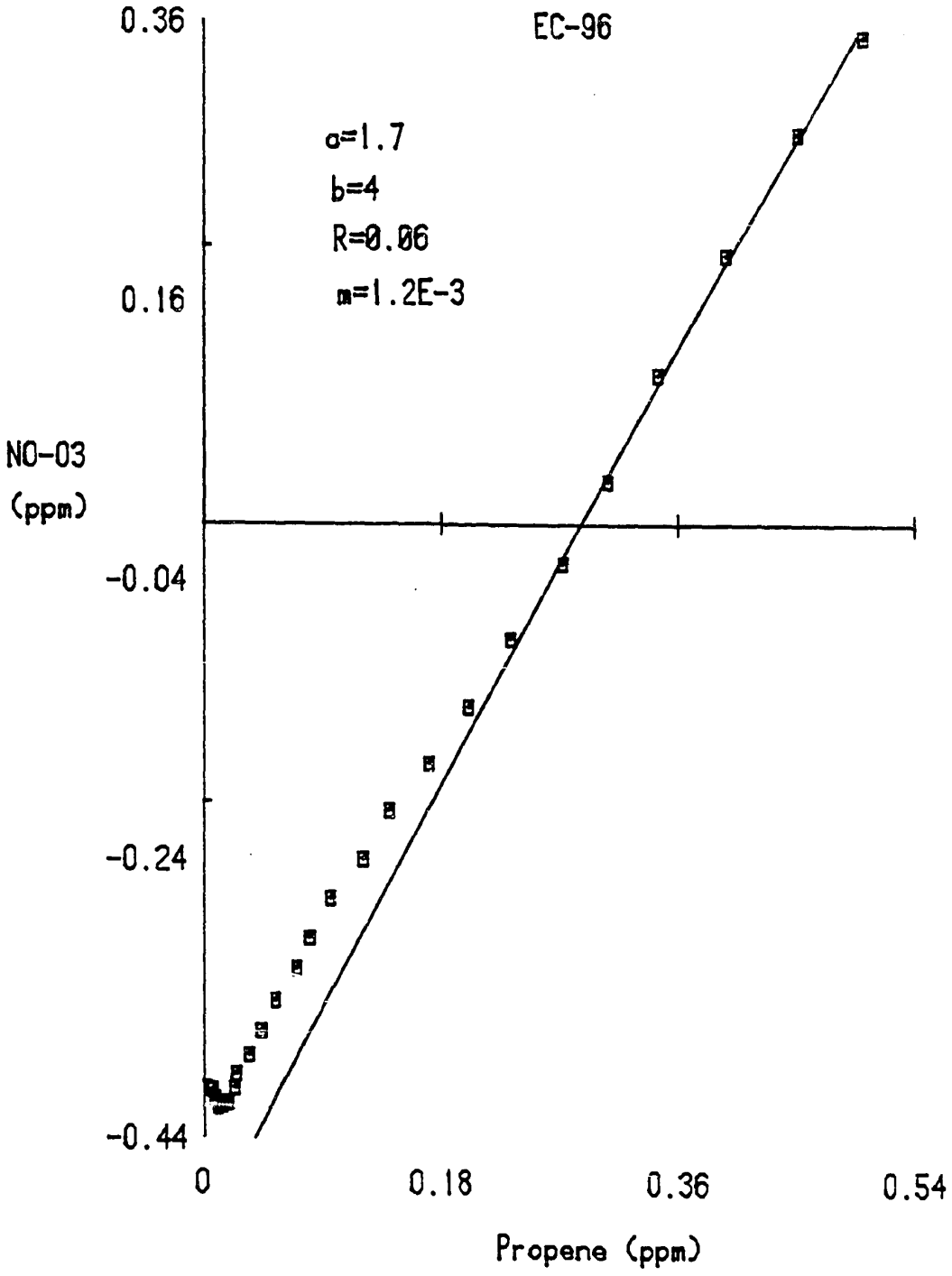


Figure 36. Simplified model prediction for EC-96.

a) Why does the model overpredict the ozone concentration ?

b) Why we were underpredicting the reactivity of the product of the propene/NOx system ?

The first problem as discussed previously was not unexpected from the NO-photooxidation model formulation, since we did not include any ozone removal paths and termination reactions, i.e., reactions which compete with reaction of RO2+NO, and prevent ozone formation. Although it is certain that the reaction of RO2+NO is a dominant path in the NO-photooxidation region, once nitric oxide is gone due to build up of ozone, competing reactions such as RO2+RO2 and RO2+NO2 become important and their contribution to the overall chemical kinetics of the system should be considered.

It was observed that at low HC/NO ratio and low NO2 concentration reaction of NO2+O has a very small contribution toward suppressing the ozone overprediction. This observation is presented in Fig. (37). In this figure we applied the NO photooxidation model with NO2+O (Eq.29) and without this reaction (Eq.19). Notice that this reaction has almost no effect in the NO photooxidation region but its contribution begins once we enter the ozone accumulation region where the concentration of NO2 has reached an appreciable amount.

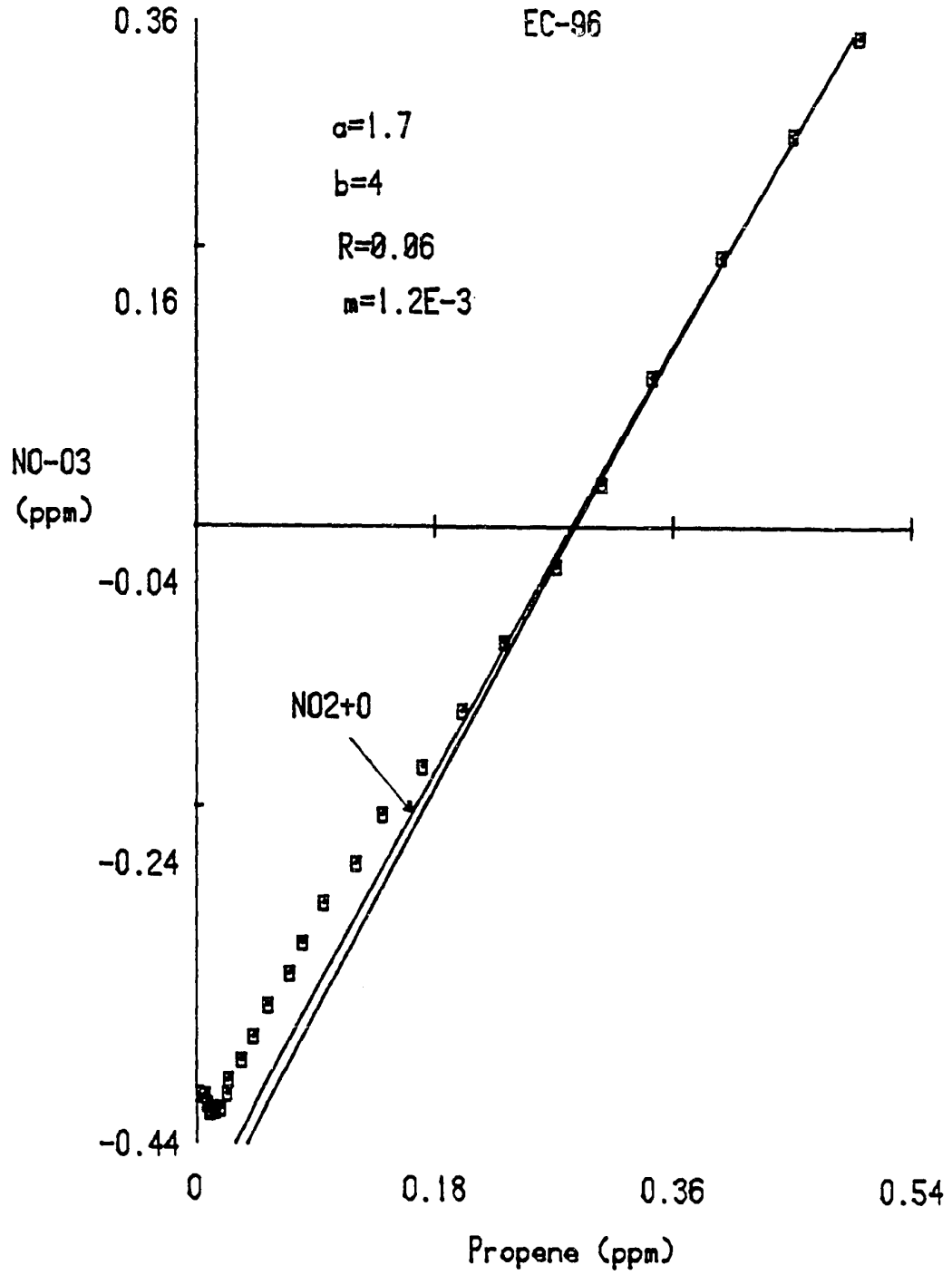


Figure 37. The effect of NO_2+O reaction on the simplified model prediction for EC-96.

Effect of Termination Reactions

In order to investigate the effect of the termination reactions we incorporated the reaction of RO2+RO2 into the model. Inclusion of this reaction leads to the addition of a quadratic term to the steady-state equation for RO2, Eq. (15-a). Also, under this condition the slope of the time independent plots became dependent on the nitric oxide concentration.

$$\frac{d[NO\text{-}O_3]}{d[HC]} = \frac{K_{NO} - K_3[NO][RO_2] + K_4[NO_2] - [O]\left\{K_5[O_2][M] - K_6[NO_2] - K_d[NO\text{-}O_3]\right\}}{K_{HC} - [HC](m + K_d)} \qquad (35)$$

$$[RO_2] = \frac{-K_3[NO] + \sqrt{K_3[NO]^2 + 4K_8\left\{m(a[HC] + bR[P])\right\}}}{2K_8} \qquad (36)$$

where k8 is the rate constant for RO2+RO2 reaction. Solution of the RO2 equation, NO = NO (HC) and NO2 = NO2 (HC) from regression analysis were inserted back into Eq. (35) and the resultant solved numerically. The graphical representation of our numerical solution is presnted in Fig. (38). In this figure the solution with and without RO2+RO2 coincide upon each other. This suggests that, the contribution of this reaction for this particular experiment is very small and can be left out. In that figure the rate constant of RO2+RO2 (k) was multiplied by 20 and 50. Notice that even

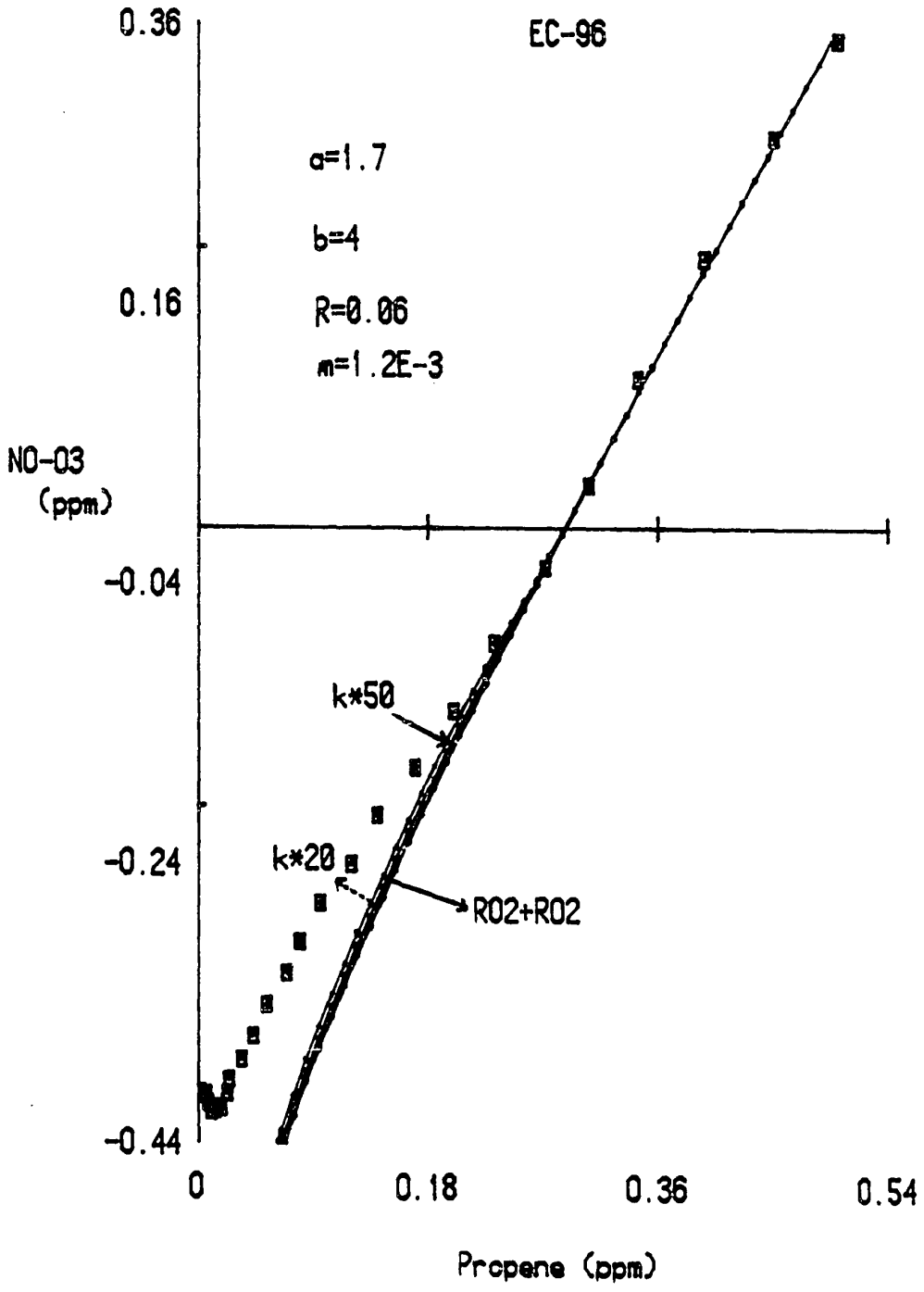


Figure 38. The effect of RO_2+RO_2 on the simplified model prediction for EC-96.

with such a high value for the rate constant there is not enough contribution to account for the observed ozone overprediction. This observation was supported with the result of the computer simulation of the detailed mechanism for the same experiment. This result will be presented shortly.

The other termination reaction which we considered was the reaction of RO2+NO2 which leads to PAN formation. To observe the effect of the reaction of RO2+NO2, we subtracted out the effect of this reaction from the y-coordinate, i.e., rather than plotting the normal variables (NO-O3) we plotted (NO-O3-PAN) vs. (propene). This approach is analogous to the sensitivity tests done by modelers which they perform computer simulation with the explicit mechanism to investigate the effect of certain reactions and parameters on the overall model's prediction (78-79).

In figure (39) the plot of (NO-O3-PAN) vs. propene for EC-96 is presented. Comparison of the results with figure (38) indicates the significance of the PAN correction. Some more examples of such plots are presented in figures (40-46) and the summary of the results are presented in table (VII). Notice in this table that all experiments predict a very small value for the reactivity parameter.

By incorporating the competing reaction with NO2 photolysis and termolecular formation of ozone, i.e., NO2+O and termination reactions (RO2+RO2 and PAN correction) we were

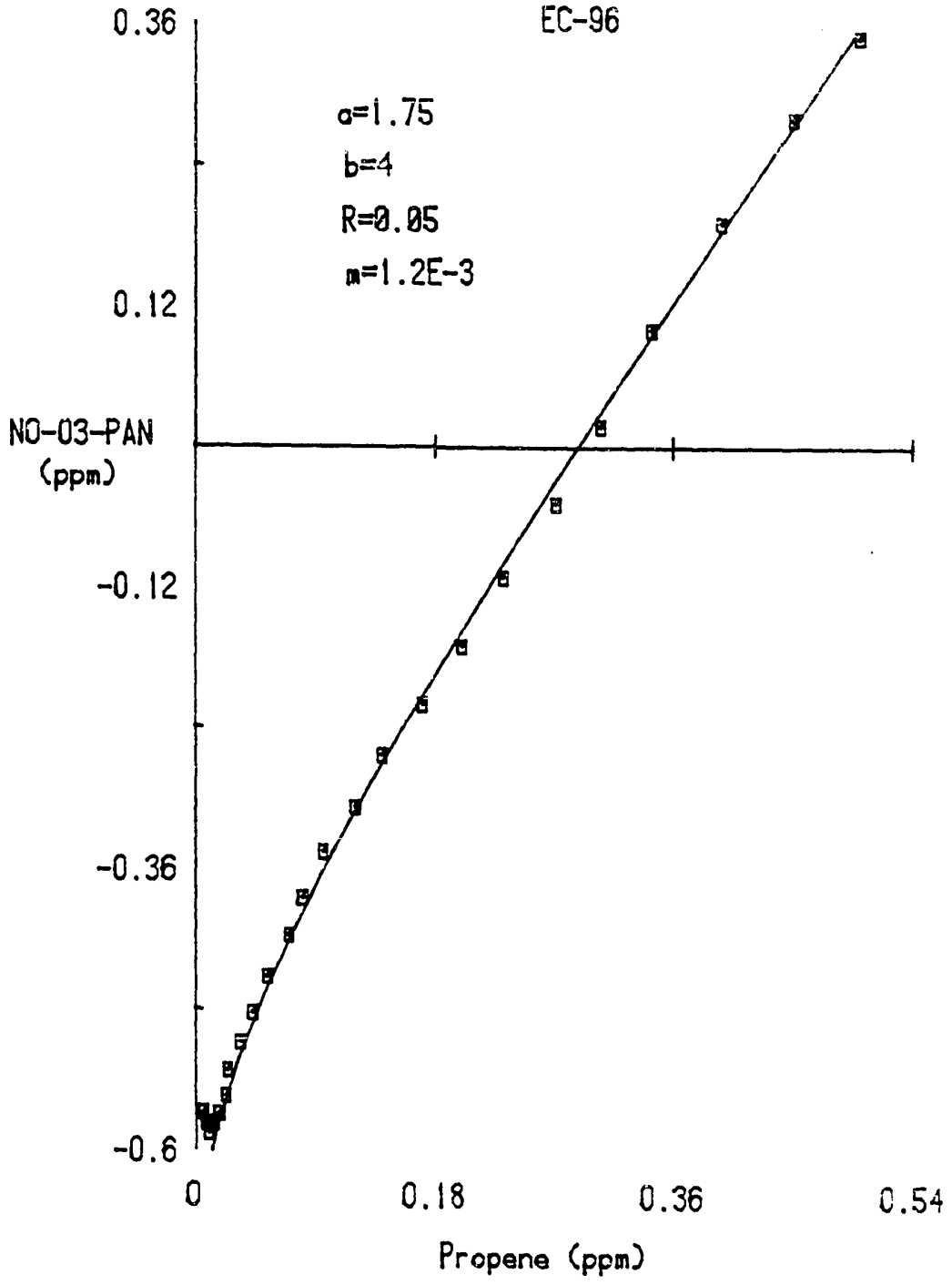


Figure 39. Effect of RO_2+NO_2 on the simplified model prediction for EC-96.

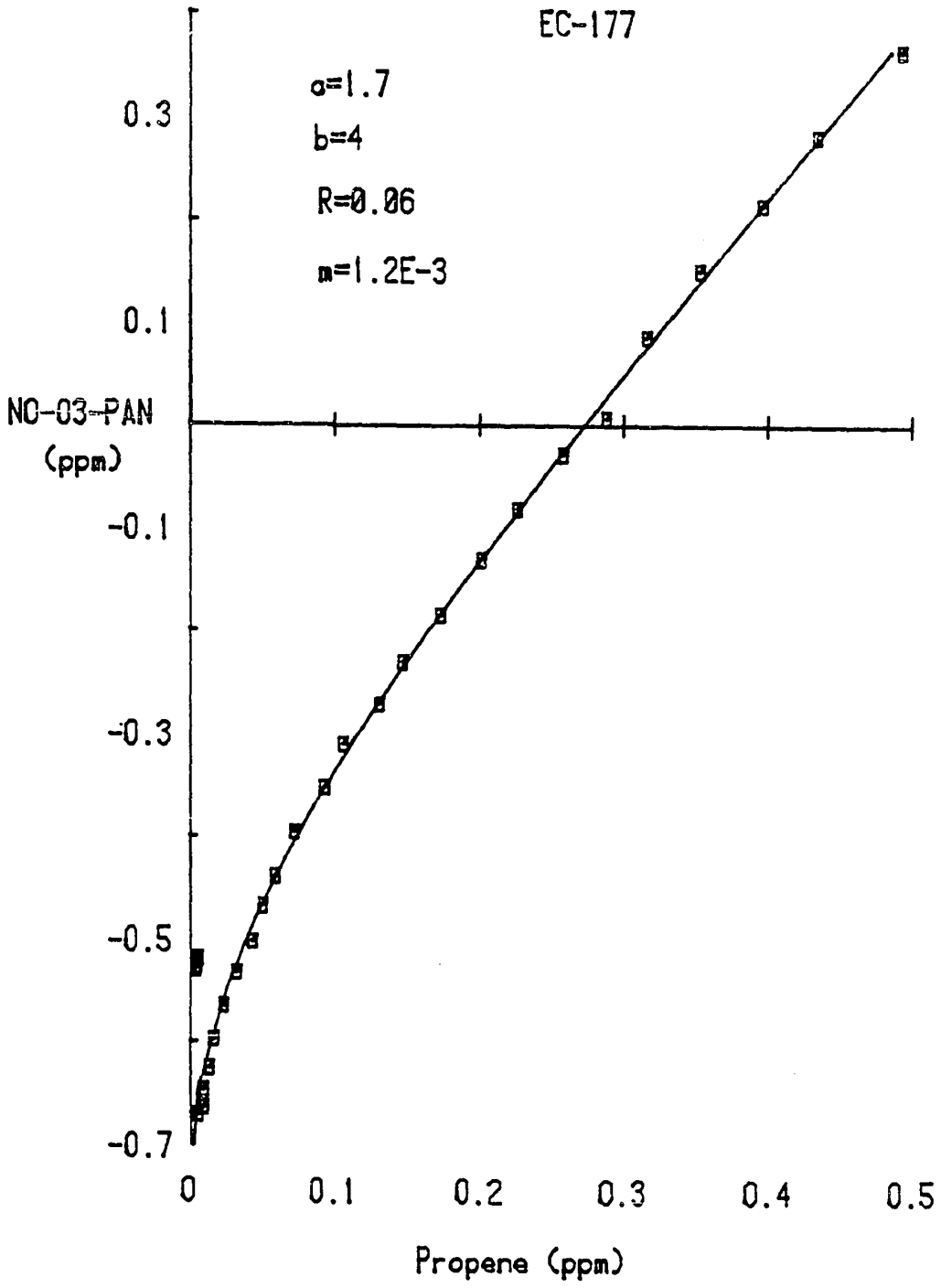


Figure 40. Simplified model prediction for EC-177.

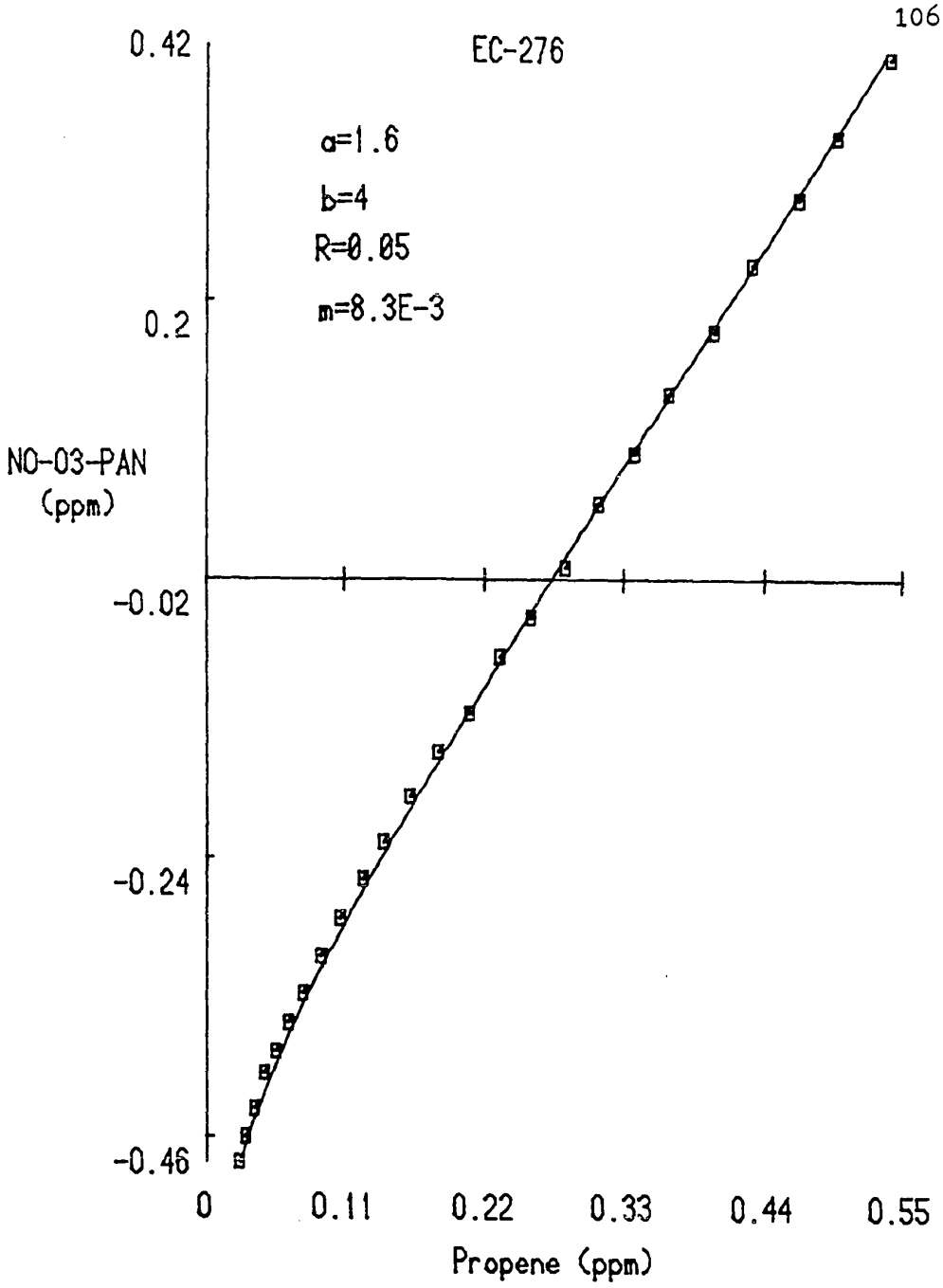


Figure 41. Simplified model prediction for EC-276.

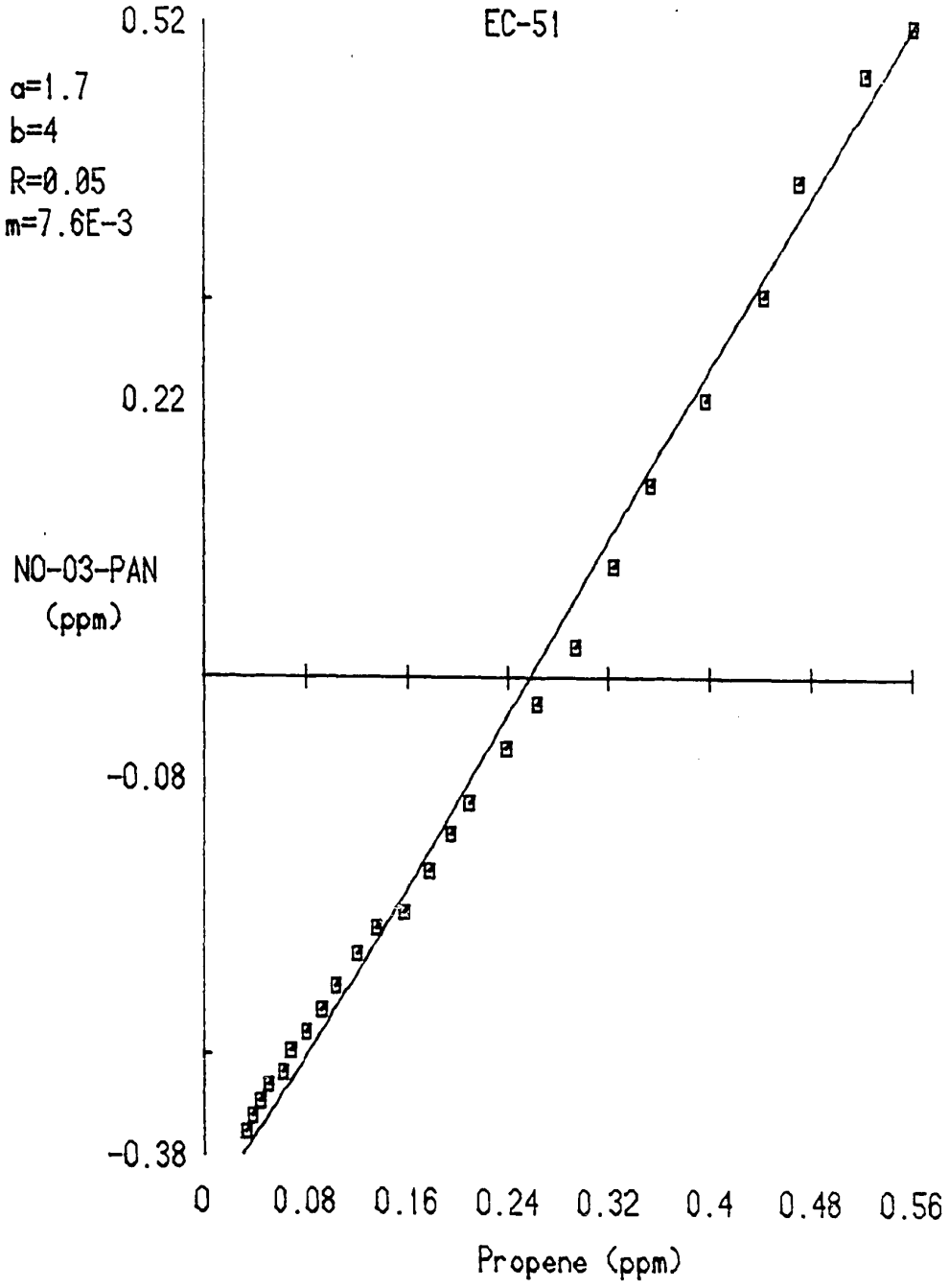


Figure 42. Simplified model prediction for EC-51.

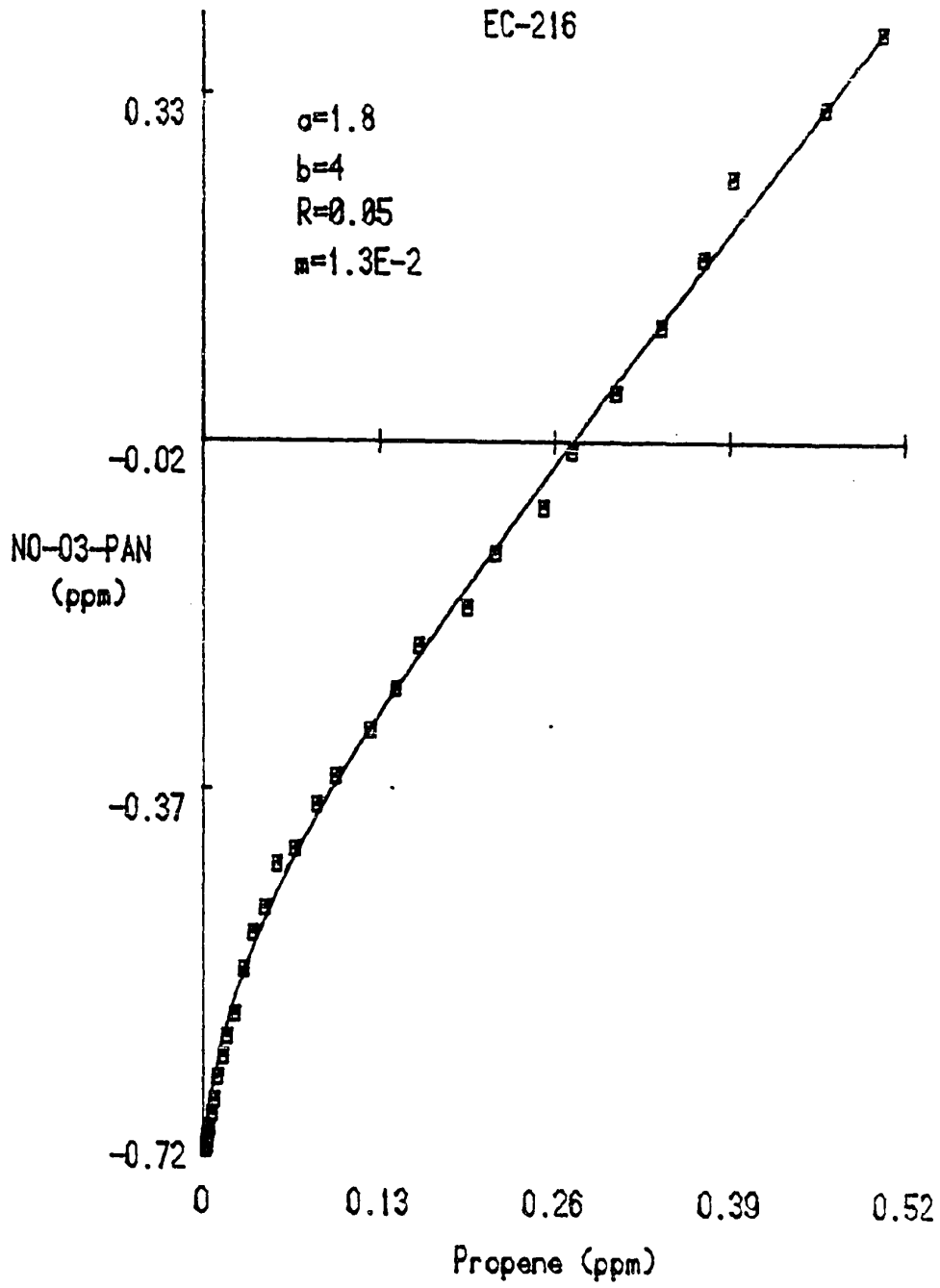


Figure 43. Simplified model prediction for EC-216.

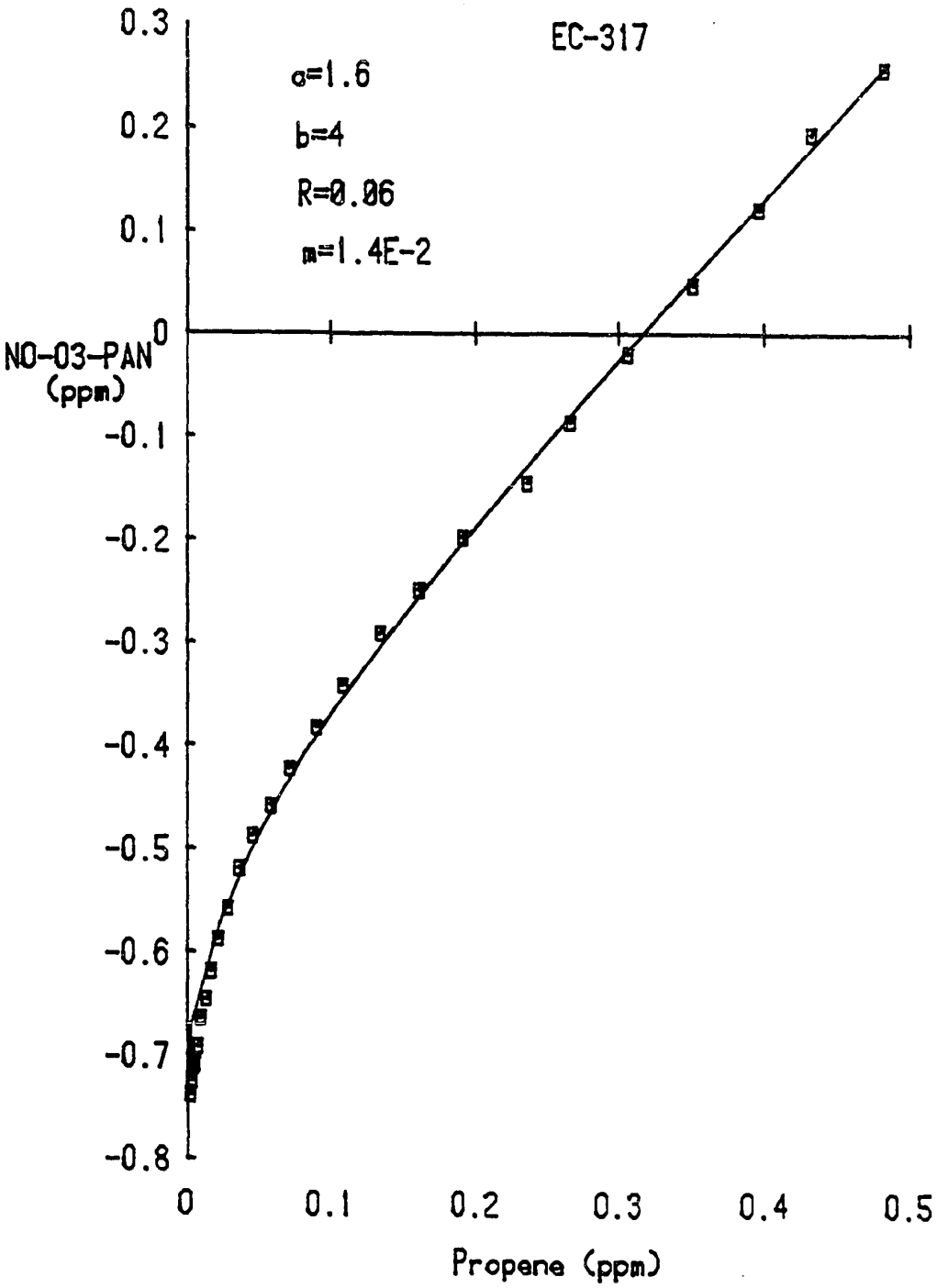


Figure 44. Simplified model prediction for EC-317.

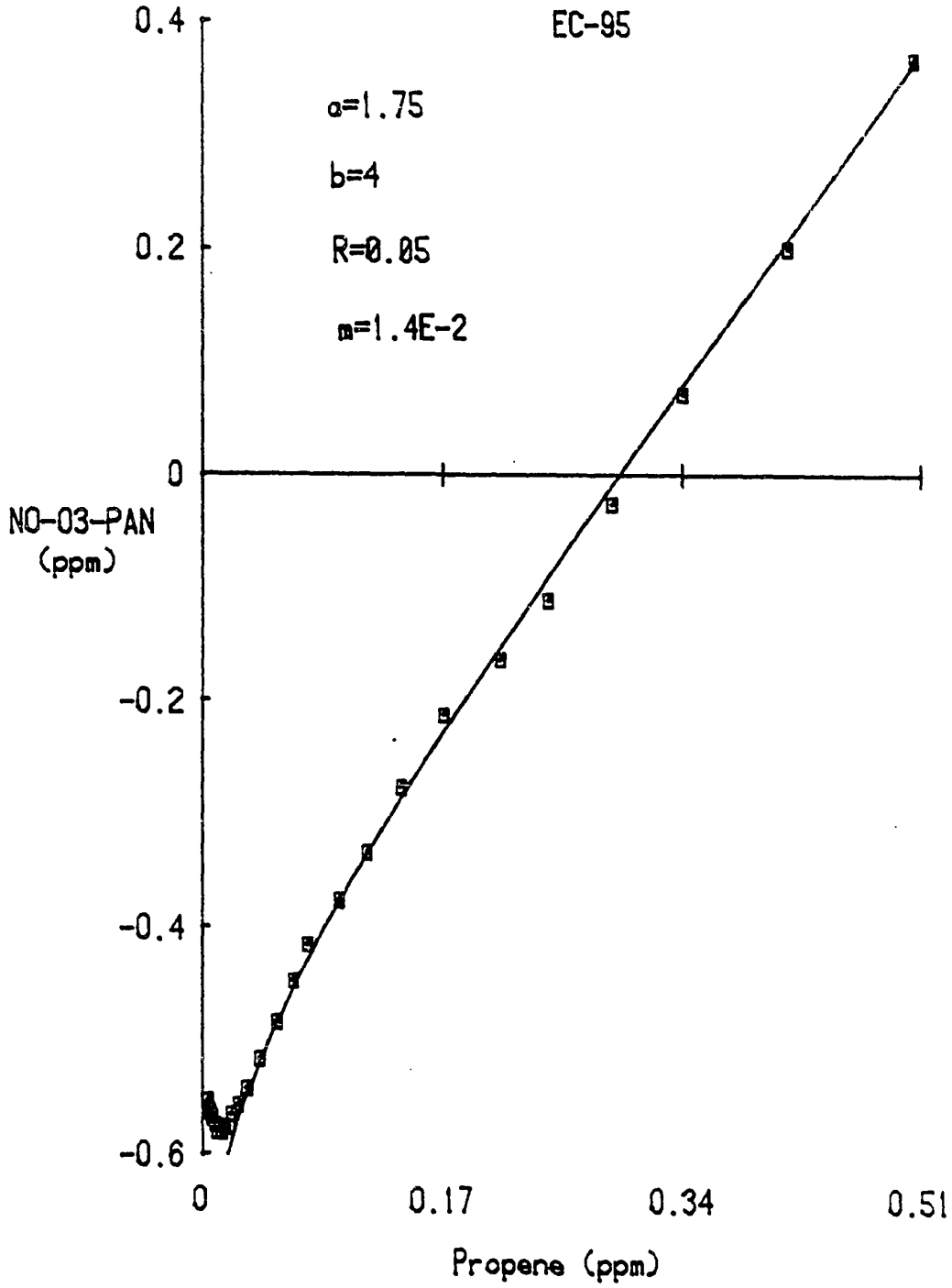


Figure 45. Simplified model prediction for EC-95.

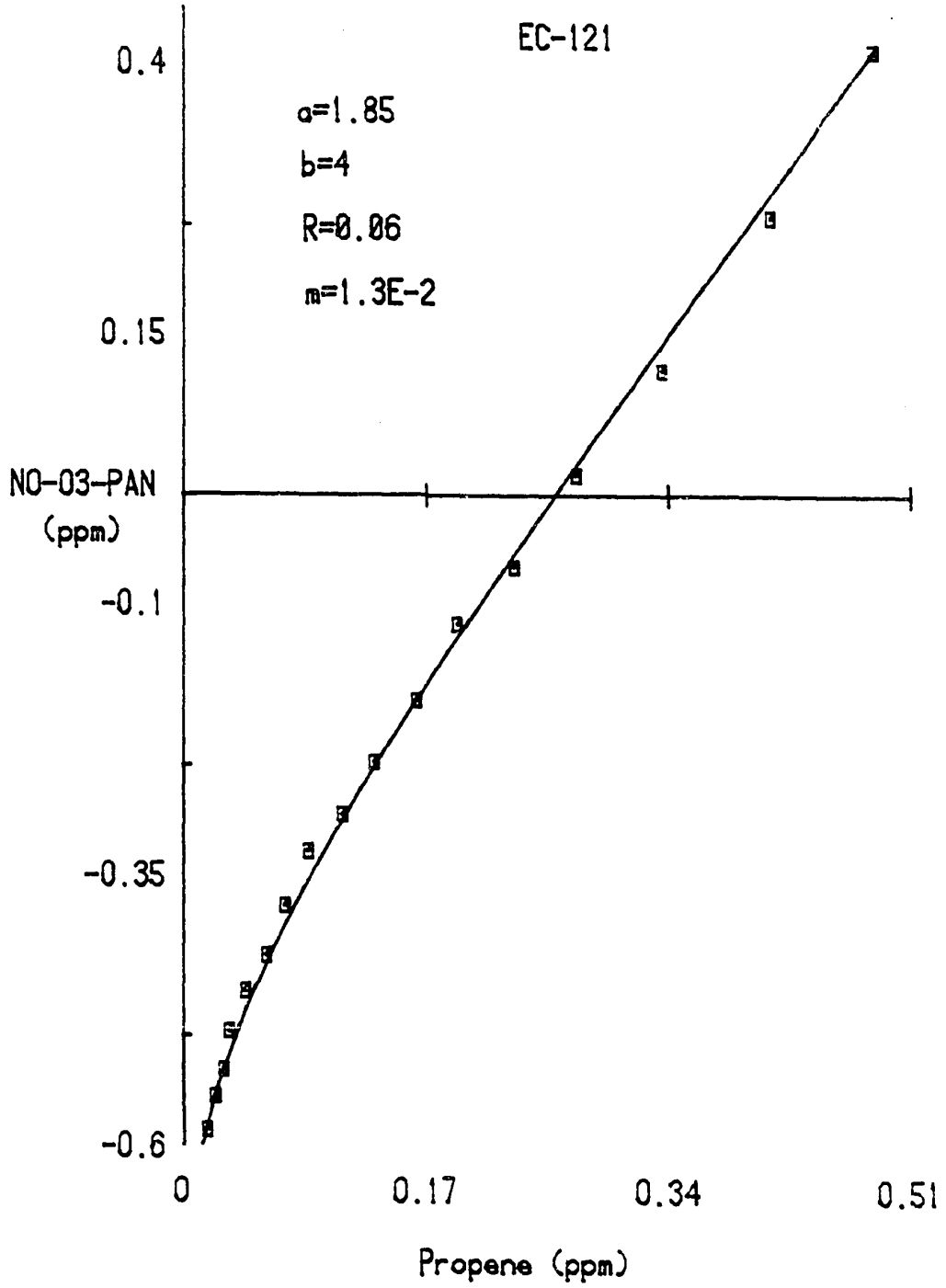


Figure 46. Simplified model prediction for EC-121.

TABLE VII

SIMPLIFIED MODEL PREDICTION RESULTS FOR PROPENE/NO_x

EC-no.	[HCl ppm	[NO] ppm	m/k	m (min)	a	b	R
96	0.500	0.349	41	1.2E-2	1.75	4	0.05
177	0.493	0.364	58	1.2E-2	1.7	4	0.06
317	0.493	0.256	55	1.4E-2	1.6	4	0.06
95	0.504	0.365	44	1.4E-2	1.75	4	0.05
121	0.483	0.410	43	1.3E-2	1.85	4	0.06
276	0.540	0410	28	8.3E-3	1.6	4	0.05
51	0.552	0.516	32	7.6E-3	1.7	4	0.05
216	0.503	0.412	42	1.3E-2	1.8	4	0.05

able to mimic the behavior of the experimental data very closely in both the NO-photooxidation and ozone accumulation regions. However, we were still underpredicting the reactivity of the product of the propene/NOx system.

In order to resolve this problem, i.e., the small value of R ($R \approx 0.05$ rather $R \approx 0.5$) we looked into the effect of the reaction of propene and ozone. As mentioned earlier and also reported elsewhere (80), the role of the reaction between alkene and ozone is an unresolved issue, i.e., does this reaction make "excess" ozone or does it serve as a sink for ozone.

To examine the possible effect of the reaction of the propene and ozone we integrated the detailed mechanism for the propene/NOx system provided by Carter et al (42) with the CHEMK program. CHEMK is a Fortran based computer program which, when given a chemical kinetic mechanism, computes the concentration of various species in time (77). That version has been modified such that besides the concentration-time profile, information on the rate of elementary reactions in descending order of significance is printed along with the net reaction rates. Also in this version the "initial guess" for starting the numerical integration and "error limit" for convergence test criteria have been optimized such that the least amount of execution time (CPU) is required. For a detailed discussion of the modified version refer to appendix (B).

In order to investigate the effect of the reaction of propene and ozone we performed experiments in which we turned "on" and "off" the reaction of propene and ozone. In the "on" experiment all reactions as proposed were included (42). This run had the same initial conditions as EC-96 (76). The predicted value for a, b and R for the EC-96 simulated data were 2, 4 and 0.05, Fig (47). Notice that the computed reactivity parameter from the explicit mechanism also is very small number. In order to observe the effect of the RO2+RO2 reaction, the product of this reaction, i.e., H2O2, was subtracted out from y-coordinate Fig (48). Comparison of the model with H2O2 subtracted Fig (48) and without H2O2 substracted Fig (47) indicates that the reaction of RO2+RO2 will provide a negligible correction. This result is in agreement with our previous observation where we corrected the model by incorporating the RO2+RO2 reaction. One more example of a computer simulation for EC-177 is presented in Fig. (49). The small predicted value for R agrees with our previous observations. In the second experiment ("off") all reactions except the reaction of propene+O3 were included. This reaction was left out by equating its rate constant to zero. The result of the run for EC-96 is presented in Fig. (50). Comparison of the calculated parameters for these two experiments reveals that the experiment without the reaction of propene+O3 agrees with the higher theoretical value for

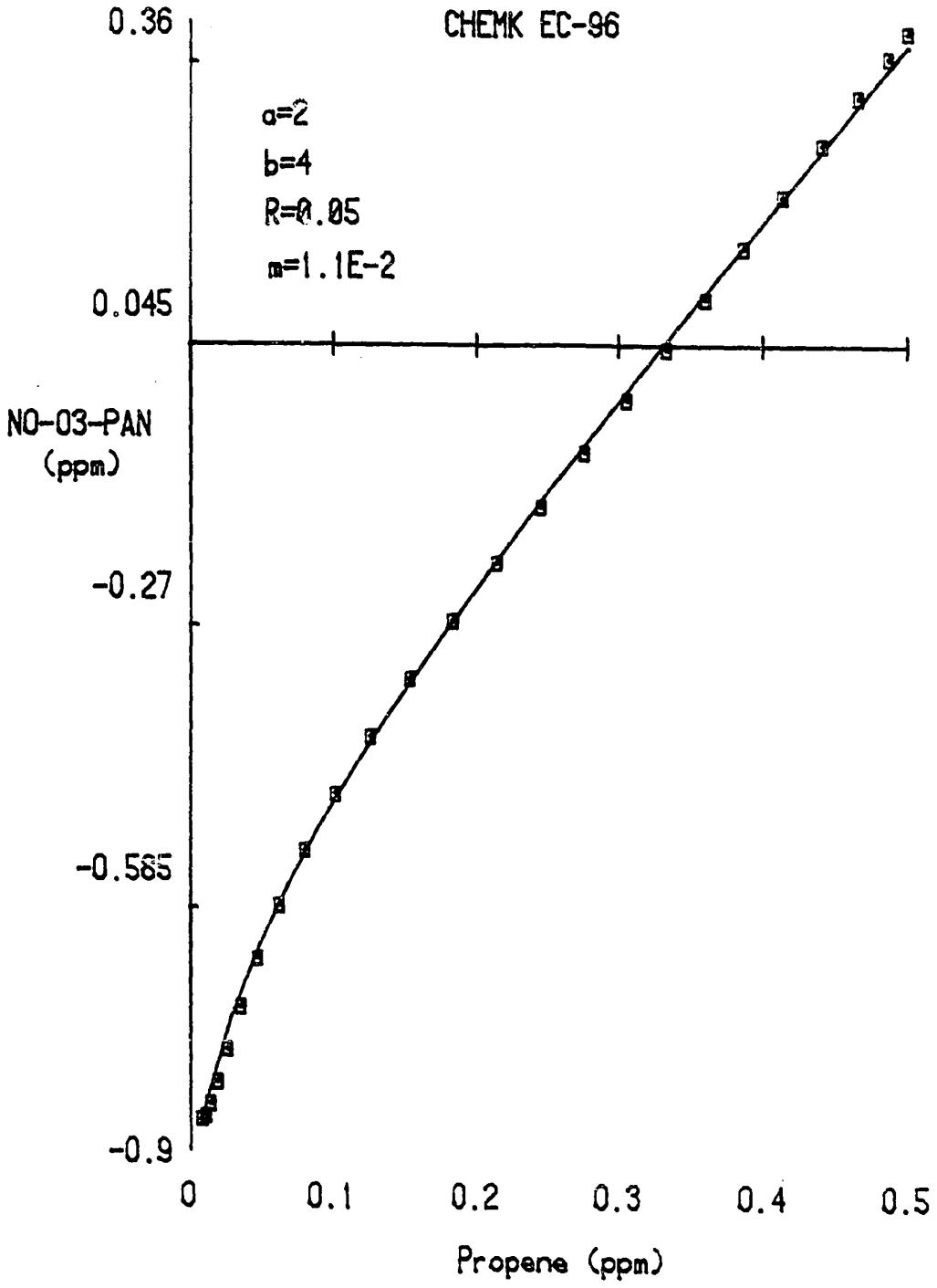


Figure 47. CHEMK computer simulation for EC-96.

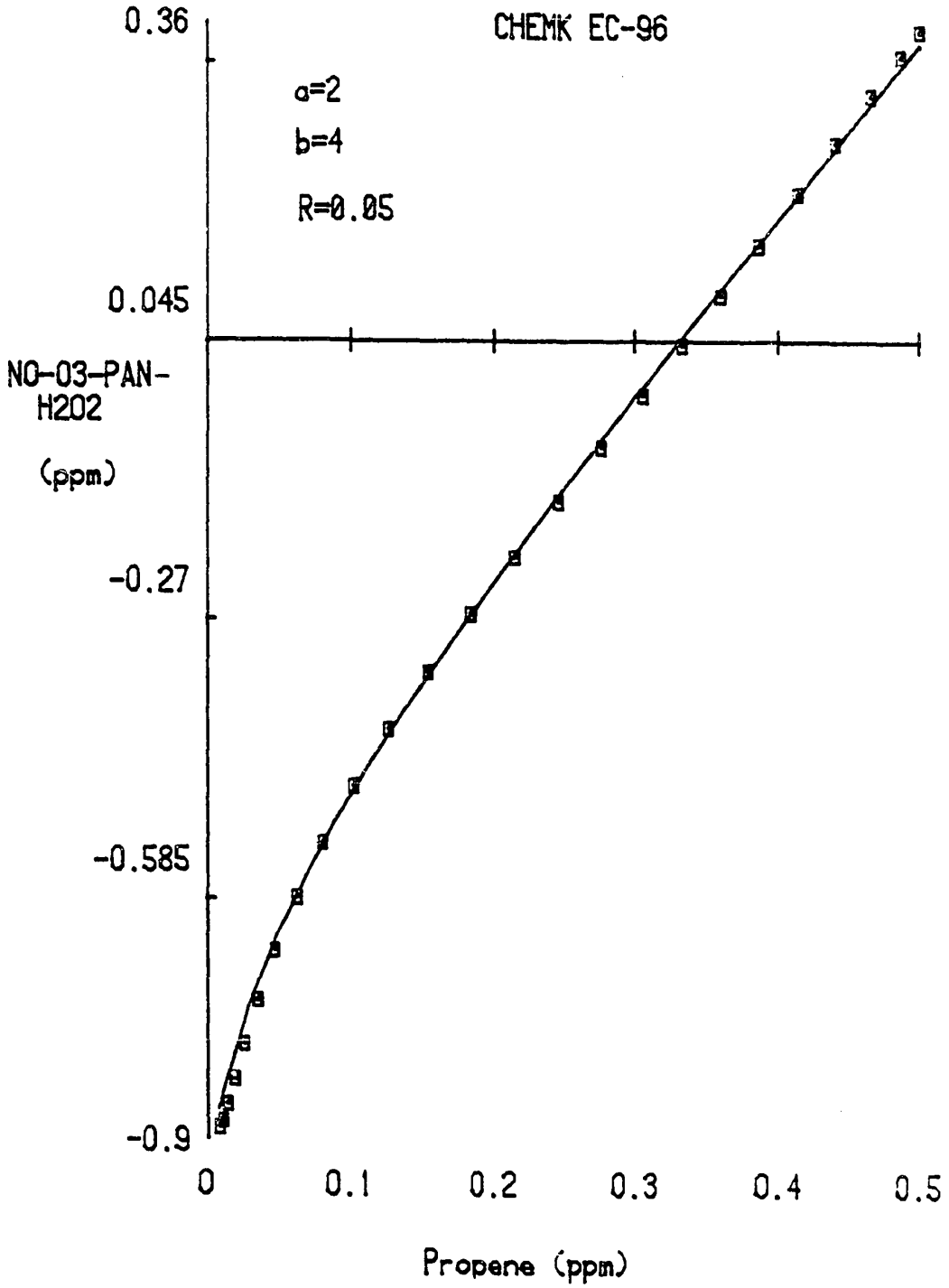


Figure 48. Effect of RO_2+RO_2 on the CHEMK simulation for EC-96.

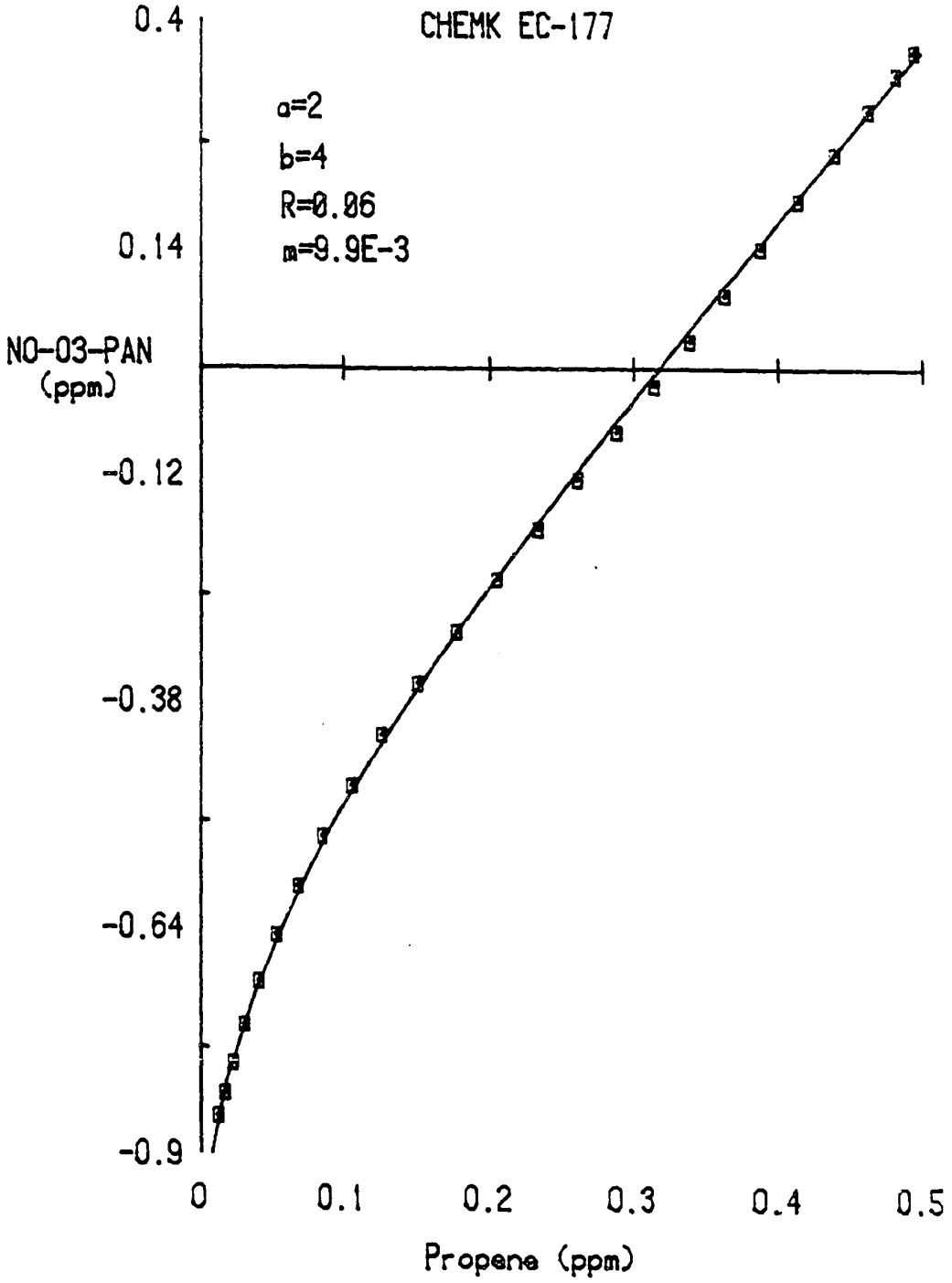


Figure 49. CHEMK computer simulation for EC-177.

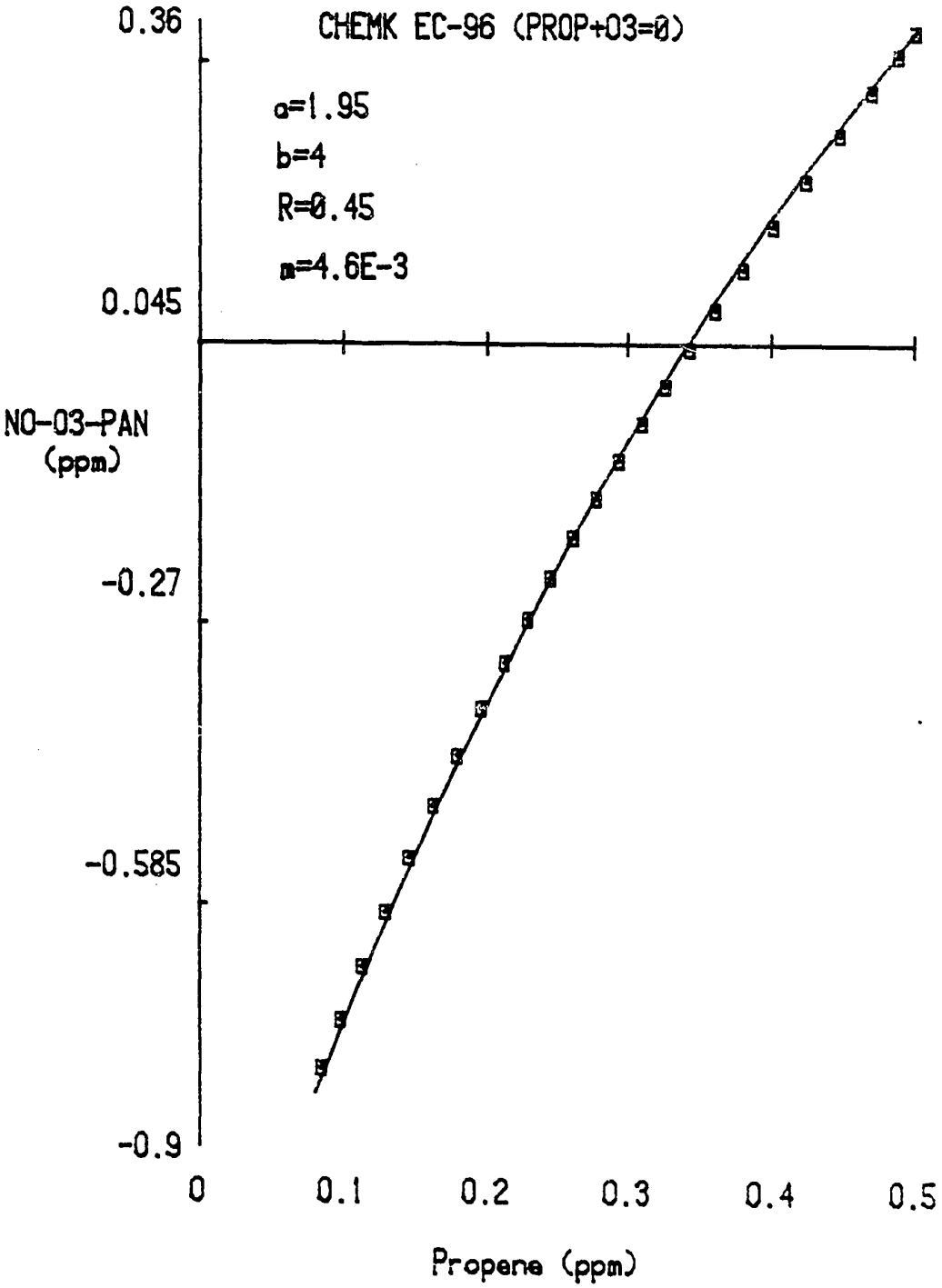


Figure 50. Effect of the propene+O_3 reaction on the CHEMK simulated data for EC-96.

"R". The recovery of the value of "R" supports our previous observation obtained at low HC/NO ratios where the contribution of the reaction of propene and ozone can be left out. This recovery is intuitively correct, since we defined "R" as the relative reactivity of product with respect to hydrocarbon. The reactivity adapted as the removal rate of hydrocarbon by OH. In the case of propene which is removed by both OH and ozone, reaction of O3+propene will increase the reactivity of hydrocarbon thereby resulted in smaller value for "R". The results obtained from these on/off experiments indicate that first, the simplified model was behaving properly and the reaction of the propene and ozone which was left out from NO-photooxidation model formulation was responsible for underpredicting the product's reactivity. Second, close inspection of the computer simulation results revealed that the reaction of propene and ozone indeed acts as sink rather than a source for ozone.

VI-e Effect of Dilution for propene/NOx

In order to investigate the effect of the dilution on the predicted results for the propene/NOx system, the dilution rate was varied. Results of such experiments are presented in Figure (51). In this figure "k" is the reported value for the rate of dilution(76). It was observed that for the propene/NOx system the model is much less sensitive to the rate of dilution. This result seems correct intuitively since propene (as opposed to n-Butane) is a very reactive hydrocarbon and as a consequence has relatively much shorter chemical life time, i.e., larger value for the ratio of m/k. This ratio in essence is a measure of the relative reactivity (chemical life time) of the hydrocarbon with regard to rate of dilution. For highly reactive hydrocarbon, m/k is a large number and dilution has slight contribution in the overall model's predictions. For unreactive hydrocarbon this ratio is small which implies that the contribution of the dilution is important and ignoring this term is a major oversight.

This conclusion can be expressed explicitly by looking at the analytical equation developed in chapter IV, Eq. (28). This result is presented in chapter VII.

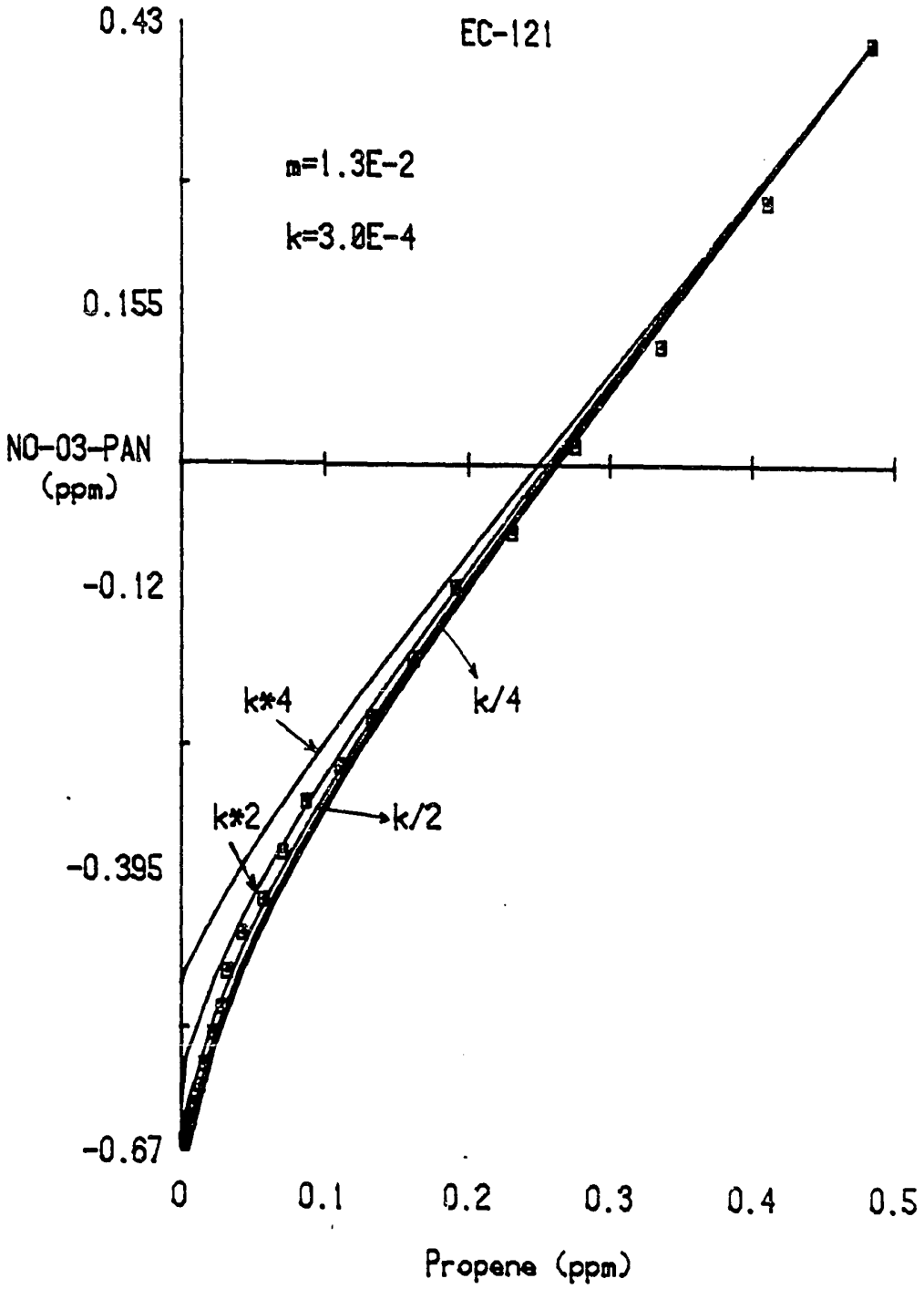


Figure 51. Effect of dilution on the simplified model prediction for propene/NO_x EC-121.

VI-f Application of Model to other HC/NOx system

The simplified model has been applied to some other HC/NOx systems. The results of such applications are presented below and also summarized in table (VIII).

i) Butene-1/NOx

The results of the simplified model for Butene-1/NOx are presented in Figures (52-54). Notice in the figures and table (VIII) as the HC/NO increases, the model predicts a smaller value for R. Increase in the HC/NO implies that ozone will be reach an appreciable concentration sooner and consequently result in a lower value for R. This result is in agreement with our previous observation for the propene/NOx system. Since Butene-1 also reacts with ozone, a reduced value of R is necessary. Therefore, the higher value of "R" will represent the true rectivity (free of ozone perturbation) and the lower value is an effective rate parameter for this system.

ii) Trans-2-Butene

The model's predicted result for Trans-2-Butene were $a=1.55\pm0.05$, $b=6$ and $R=0.03$, Figures (55-57).

It was observed that the model became sensitive to the product of "b" and "R". This features can be seen in Figures (58-60). Notice that for a given experiment as long

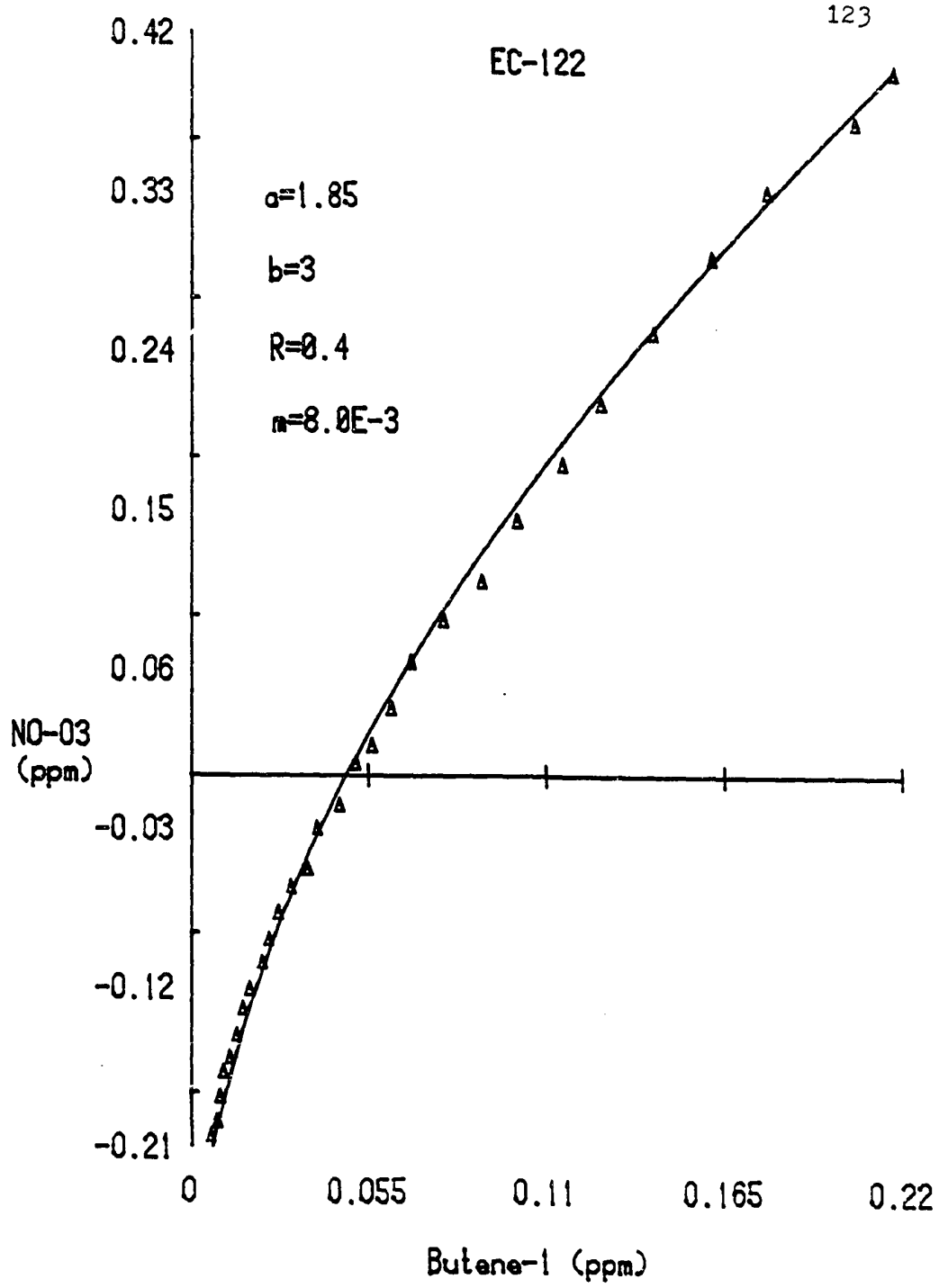


Figure 52. Simplified model prediction for EC-122.

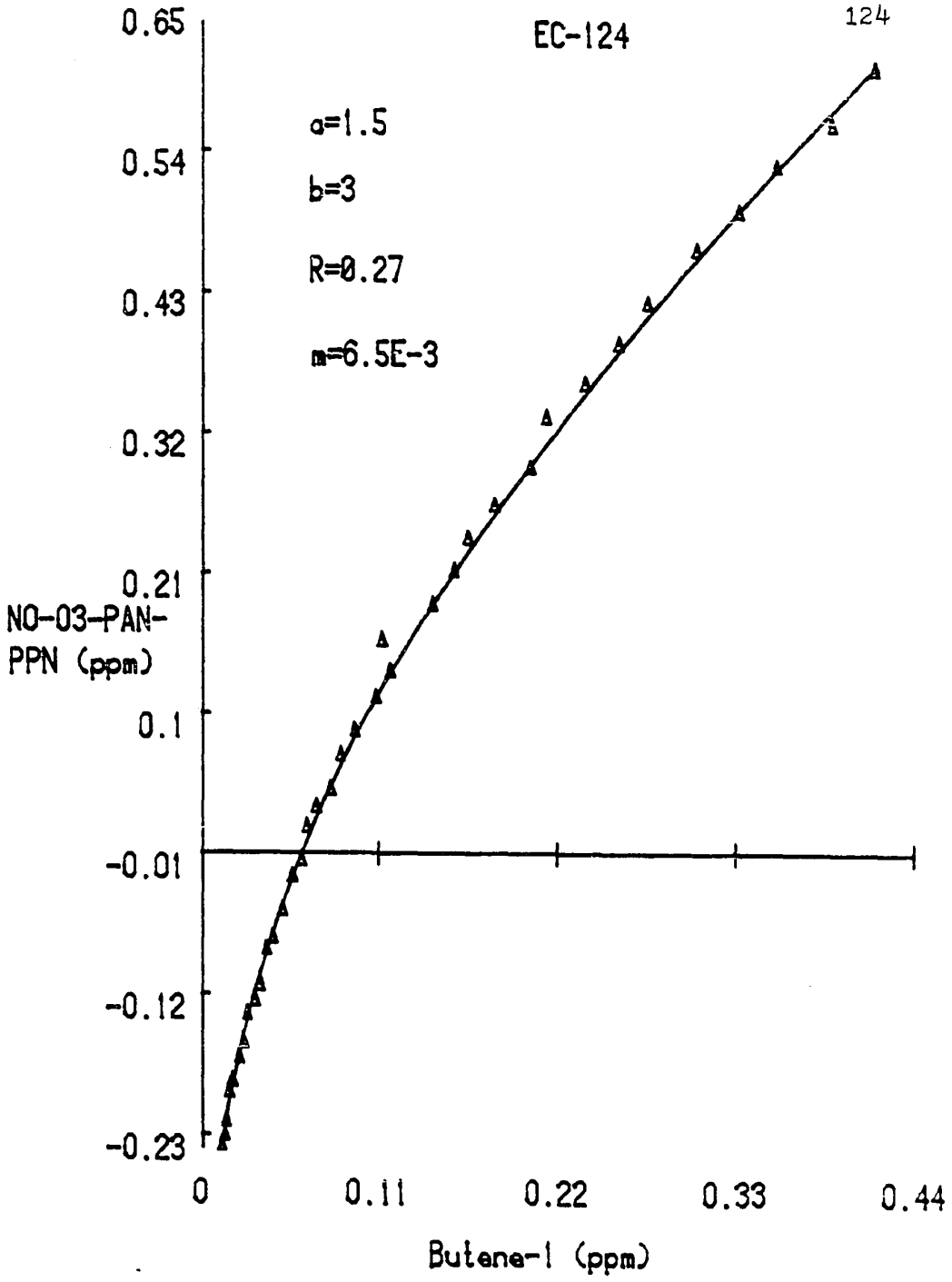


Figure 53. Simplified model prediction for EC-124.

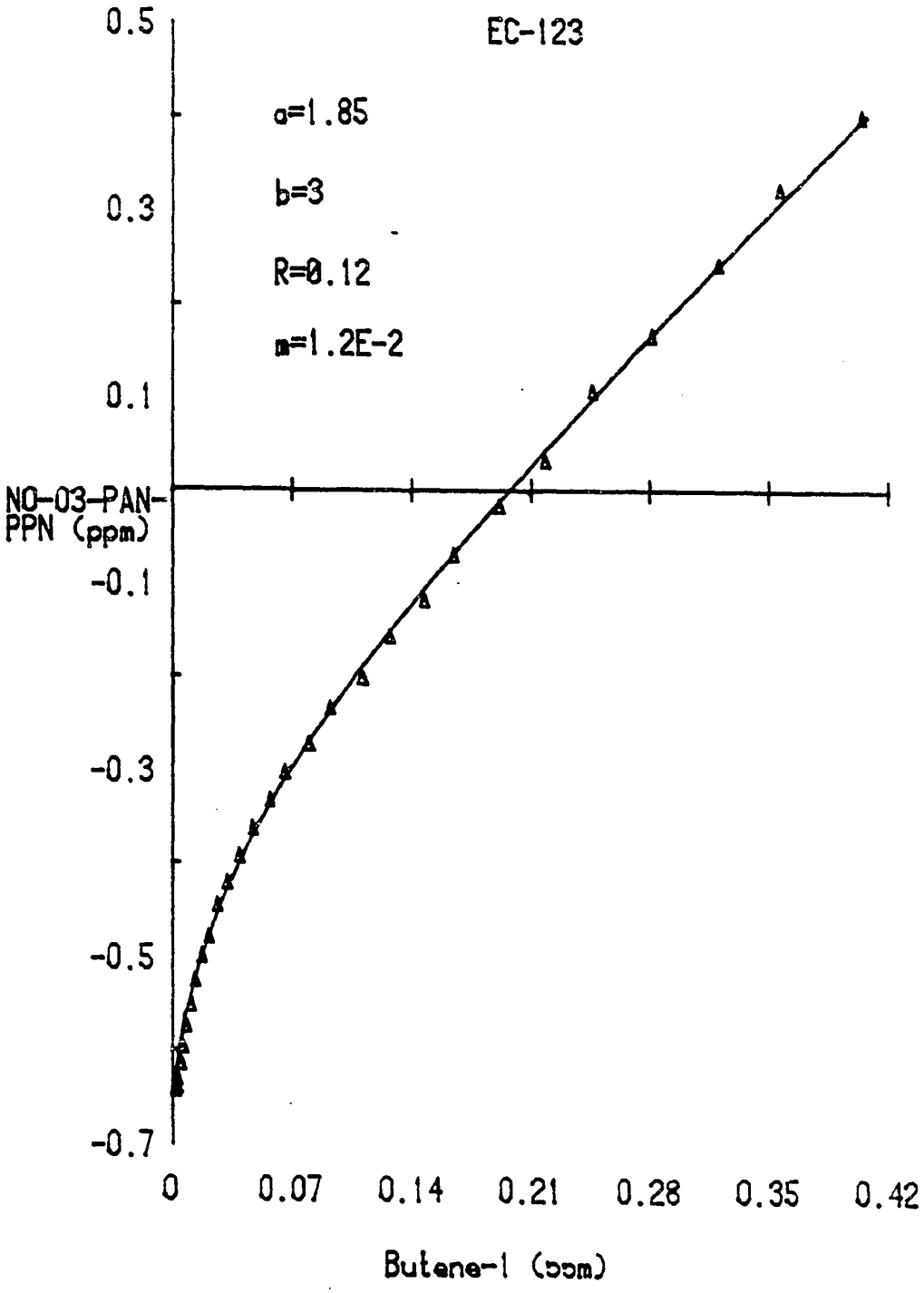


Figure 54. Simplified model prediction for EC-123.

TABLE VIII

APPLICATION OF THE MODEL TO SOME OTHER HC-NOx SYSTEMS

EC-no.	[HCl ppm	[NOl ppm	m/k	m (min)	a	b	R
122	0.217	0.398	27	8.0E-3	1.85	3	0.4
124	0.424	0.608	20	6.5E-3	1.50	3	0.27
123	0.404	0.401	38	1.2E-2	1.85	3	0.12
146	0.231	0.385	130	3.9E-2	1.55	6	0.035
147	0.417	0.782	100	3.1E-2	1.5	6	0.025
157	0.216	0.397	95	3.8E-2	1.6	6	0.03
146	0.231	0.385	130	3.9E-2	1.55	5	0.04
147	0.47	0.782	100	3.1E-2	1.50	5	0.03
157	0.216	0.397	95	3.8E-2	1.6	5	0.04

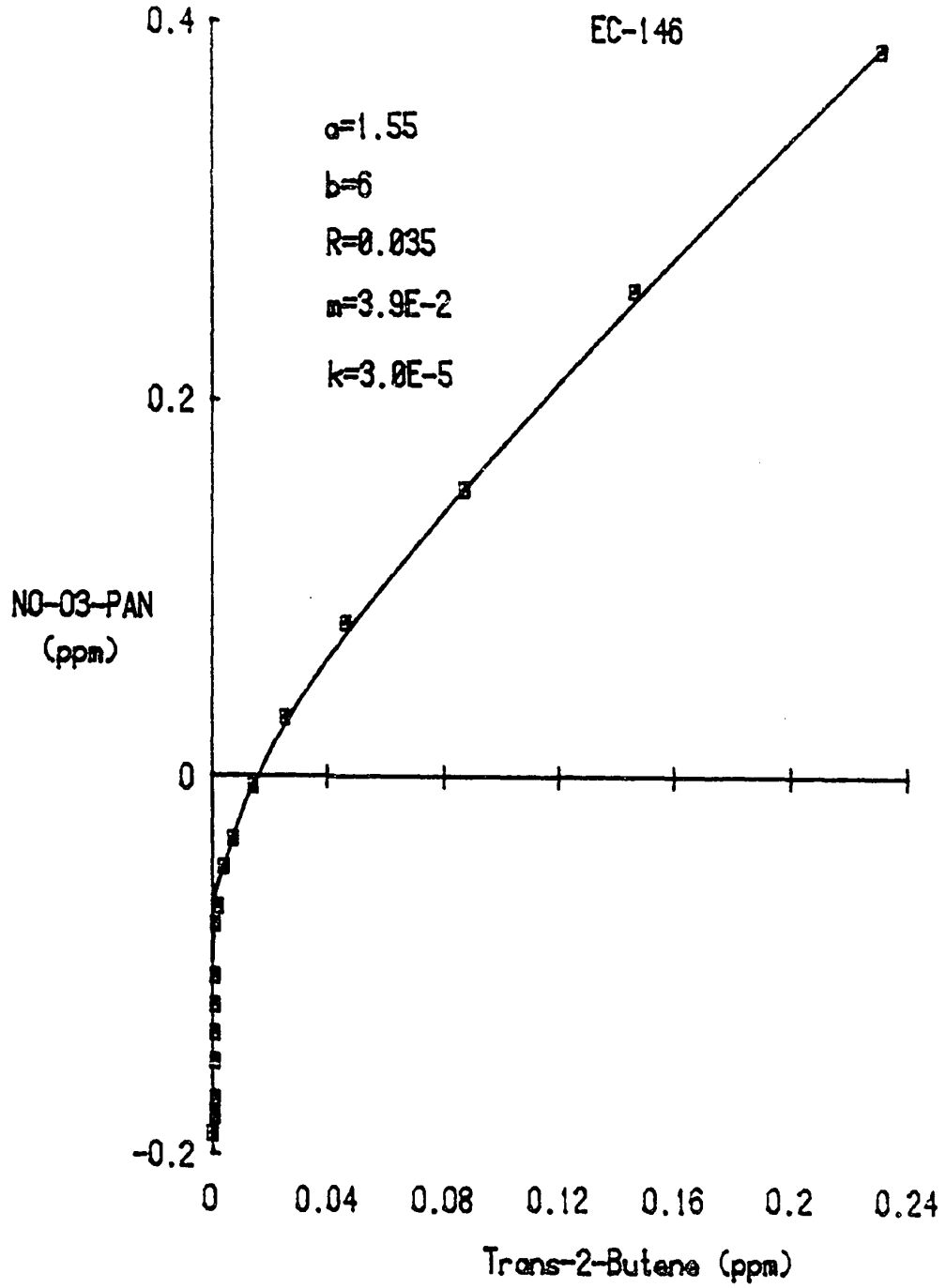


Figure 55. Simplified model prediction for EC-146.

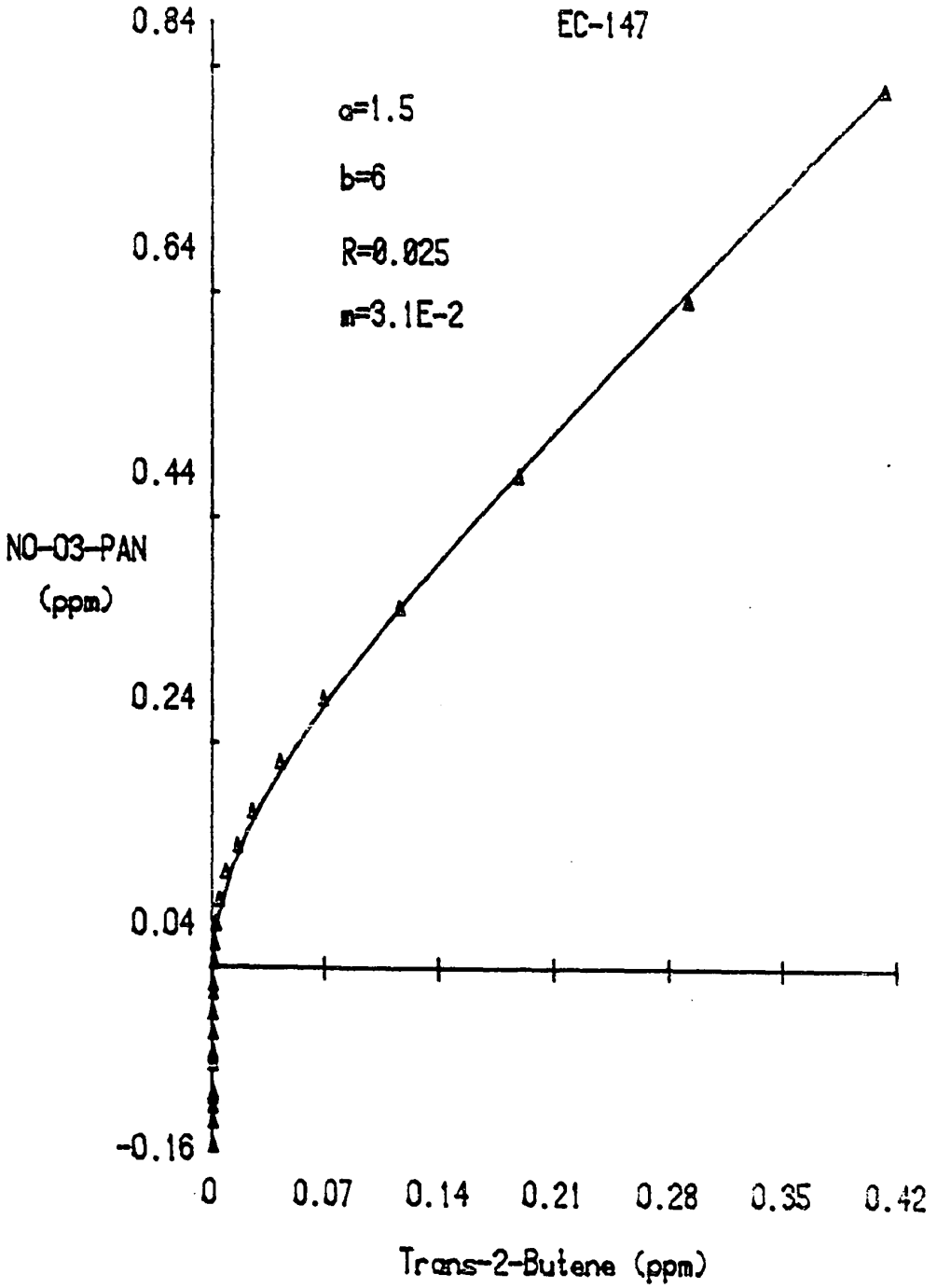


Figure 56. Simplified model prediction for EC-147.

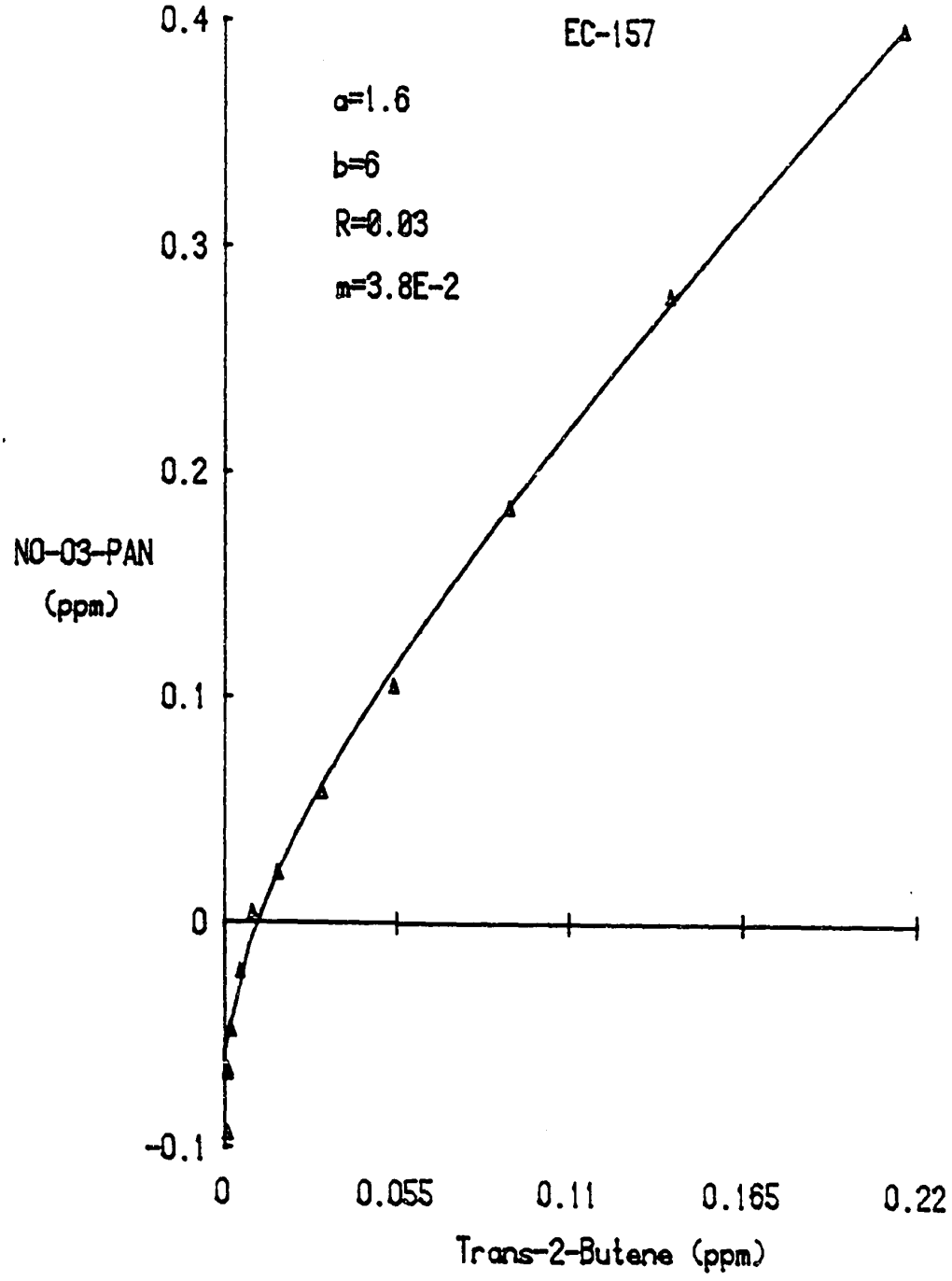


Figure 57. Simplified model prediction for EC-157.

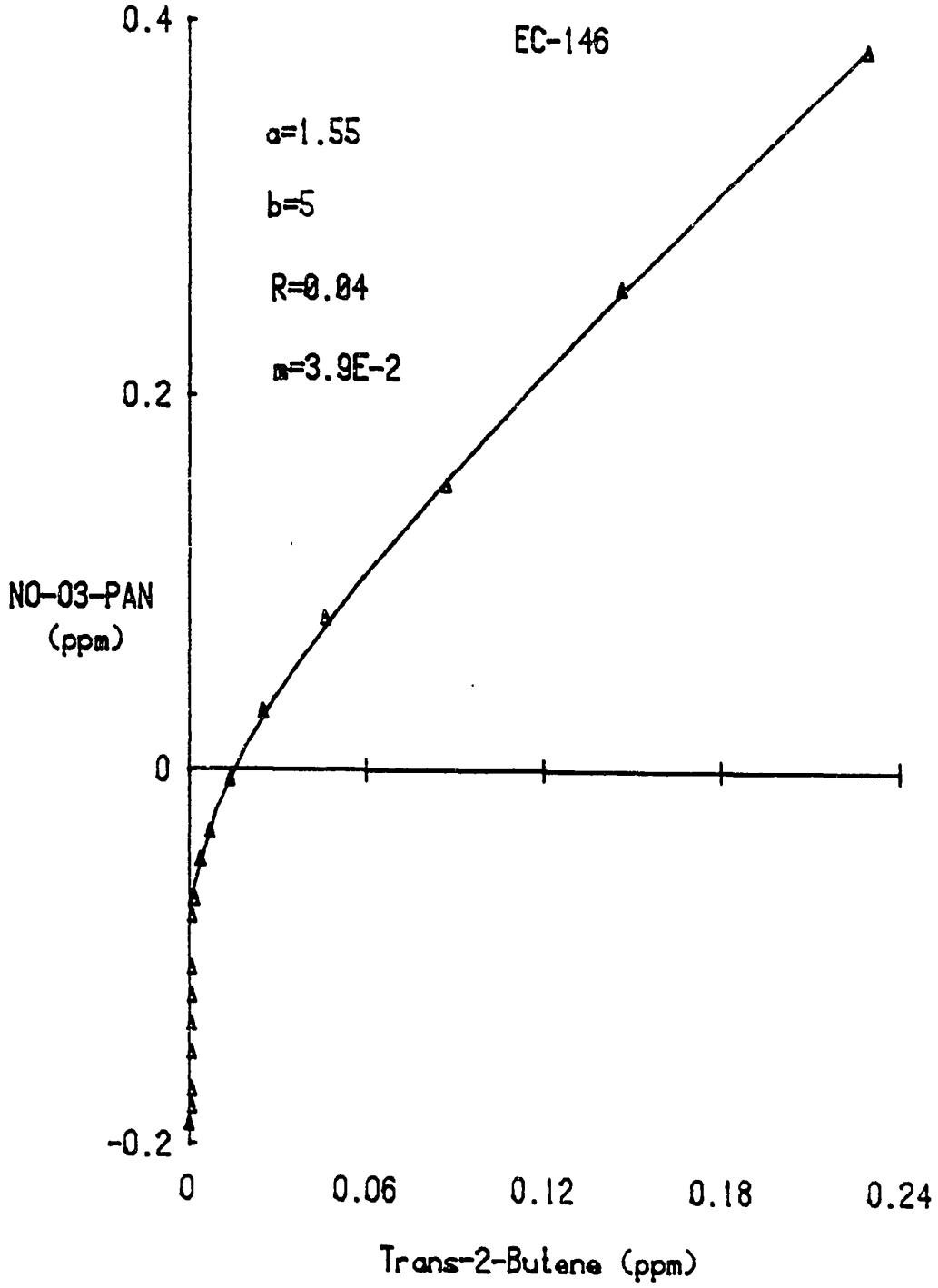


Figure 58. Simplified model prediction for EC-146.

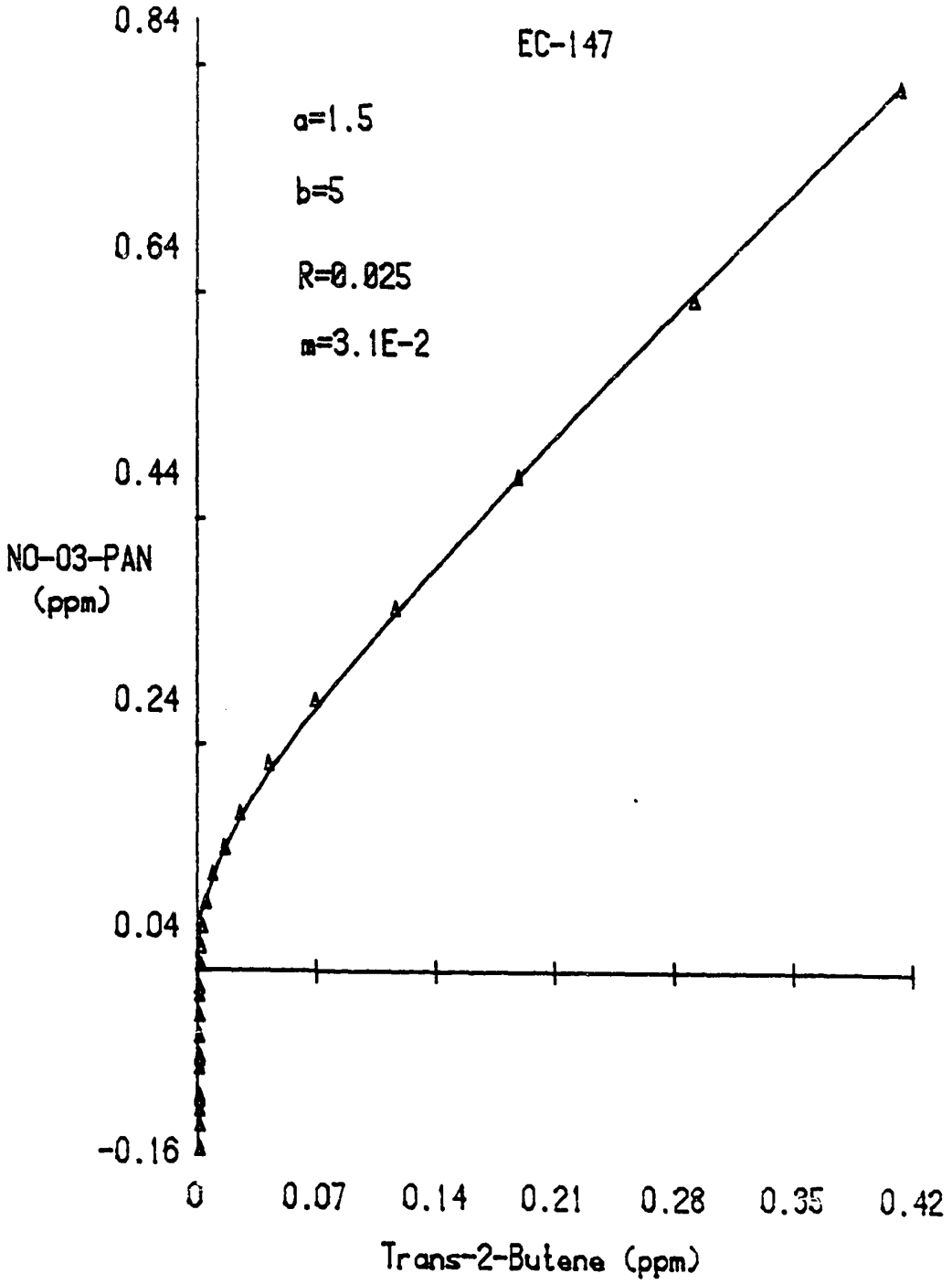


Figure 59. Simplified model prediction for EC-147.

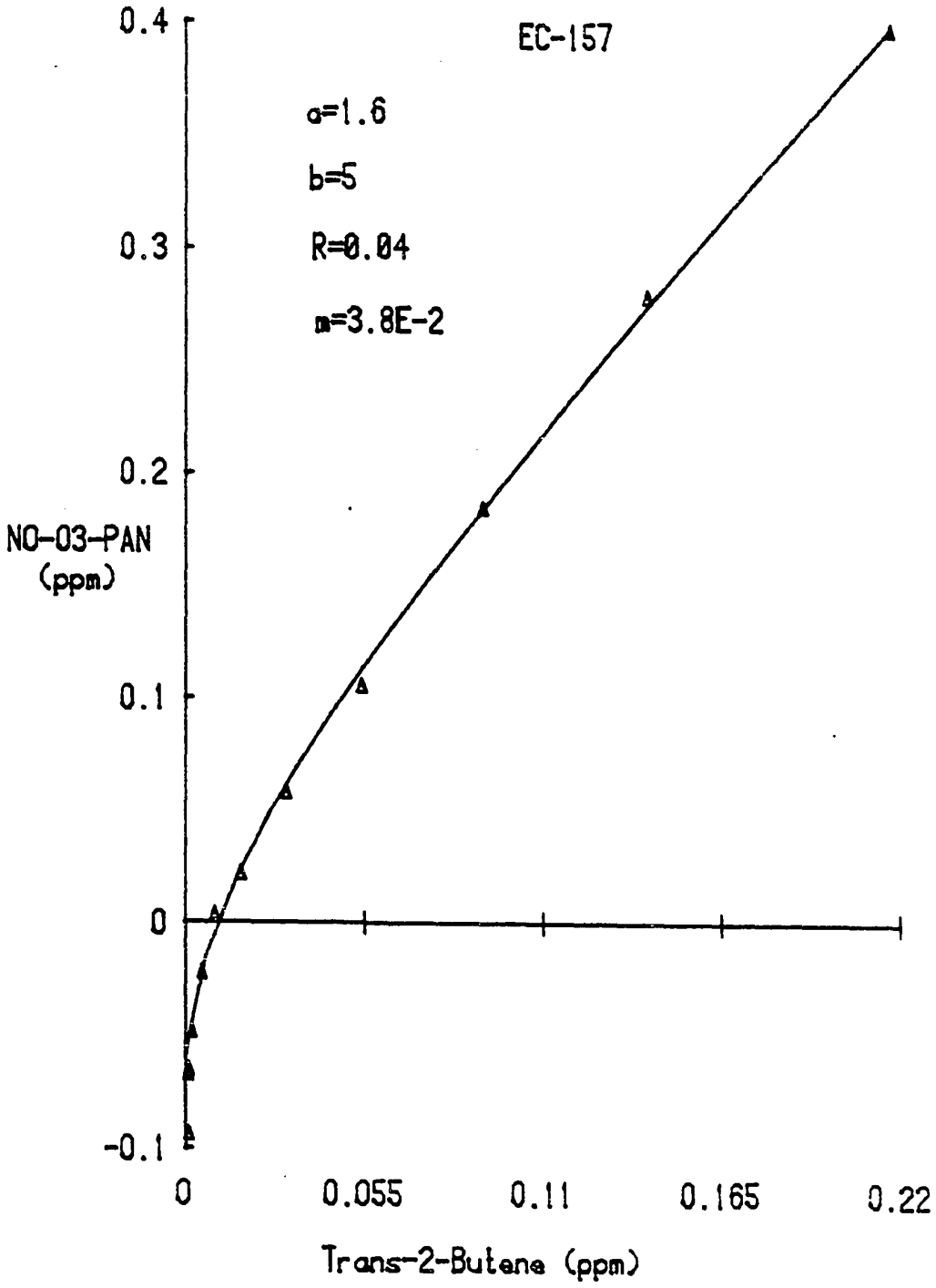


Figure 60. Simplified model prediction for EC-157.

as the product of "b" and "R" remain constant identical result will be obtained. This feature is attributed to the high reactivity of this system. Notice in the table the high value of m/k. This high value implies that Trans-2-Butene is a very reactive hydrocarbon with very short chemical life time relative to dilution. The mathematical justification for this observed interdependency of "b" and "R" is presented in chapter VII.

CHAPTER VII

GENERAL DISCUSSION AND SUMMARY

VII-a Interdependency of "b" and "R"

There are two approaches by which the experimentally observed interdependency of "b" and "R" for reactive hydrocarbons can be explained. First, considering the approximate series solution developed in Chapter IV, the simplified model can be represented in terms of "a" and "bR".

$$d[NO\text{-}O3]/d[HC] = a\text{-}bR \ln [HC]/[HC]_{\bullet} \quad (37)$$

This differential equation was obtained by leaving out the effect of dilution and also ignoring higher order terms of the expansion series. The first approximation, i.e., leaving out the effect of dilution for reactive hydrocarbon such as propene and trans-2-Butane ($m/k > 95$) is a very good assumption. To verify the accuracy of the second assumption, i.e., leaving out higher order terms of the expansion series, we integrate the approximate solution with

first order and second order term correction, i.e.,

$$d[NO\text{-}O3]/d[HC] = a - bR\{\ln(HC/HC_\bullet) + \frac{(R-1)}{2}\ln(HC/HC_\bullet)^2\} \quad (38)$$

The results of the numerical integration of the approximate solution are presented in tables (IX-X). In these tables the result of analytical equation (Eq.28), the result of numerical integration of the approximate solution with the first order correction term (Eq.37), and the result of numerical integration of the approximate solution with first and second order term correction (Eq.38) are presented in columns 2-4 respectively. In table (IX) the result of the numerical integration of [HC] vs. [NO-O3] for initial concentration of $[HC]_\bullet$ = 0.6 ppm and $[NO]_\bullet$ = 0.6 ppm are presented. In table (X) the numerical integration was performed with the identical ratio but the absolute value of the concentration changed to $[HC]_\bullet$ = 1.0 ppm and $[NO]_\bullet$ = 1.0 ppm. Also, both simulations were carried out with the rate parameters similar to the rate parameters for the propene/NOx system, i.e., a=1.8, b=4 and R=0.05.

Comparison of the results of the analytical equation (second column) with numerical integration which contains first and second order correction terms (column 4) indicates the accuracy of the approximate series solution. Comparison of the result of the approximate solution with the first order term correction (third colum) and the approximate solution with the first and second term corrections (column four)

TABLE IX

VALIDITY OF THE APPROXIMATE SERIES SOLUTION TO THE SIMPLIFIED OZONE MODEL

0.6	0.2	0.2	0.2
0.59	0.182	0.182	0.182
0.58	0.163966115974	0.163966385763	0.163966117408
0.57	0.145897209205	0.14589858266	0.145897490811
0.56	0.127792082066	0.127795996071	0.127793496619
0.55	0.109649473872	0.109658010328	0.109653488313
0.54	0.0914680563456	0.0914839875743	0.0914767951436
0.53	0.0732464286826	0.073273266543	0.0732627207466
0.52	0.0549831121444	0.0550251612456	0.055010541639
0.51	0.0366765441423	0.0367389595584	0.0367195055995
0.5	0.0183250717465	0.0184139216994	0.018388829917
0.49	-7.305544745E-5	4.927858577E-5	1.769949321E-5
0.48	-0.0185196931728	-0.0183557699425	-0.0183947352161
0.47	-0.0370168111541	-0.0368020570451	-0.0368493604373
0.46	-0.055566502683	-0.0552904509661	-0.0553471015138
0.45	-0.0741709952228	-0.0738218572976	-0.0738889255612
0.44	-0.0928326621796	-0.0923972214425	-0.0924758443685
0.43	-0.111554035996	-0.111017531299	-0.111108917575
0.42	-0.130337822754	-0.129683820192	-0.129789256153
0.41	-0.149186918492	-0.14839717008	-0.148518026245
0.4	-0.168104427499	-0.167158715071	-0.16729645338
0.39	-0.187093682863	-0.185969645287	-0.186125827143
0.38	-0.206158269633	-0.204831211119	-0.205007506344
0.37	-0.225302050989	-0.223744727924	-0.223942924751
0.36	-0.244529197918	-0.242711581224	-0.242933597483
0.35	-0.263844222963	-0.261733232471	-0.261981128148
0.34	-0.283252018745	-0.280811225473	-0.281087216839
0.33	-0.302757902082	-0.299947193548	-0.300253669121
0.32	-0.322367664734	-0.319142867549	-0.319482406175
0.31	-0.342087631979	-0.338400084868	-0.338775476273
0.3	-0.36192473054	-0.357720799584	-0.358135067832
0.29	-0.381886567714	-0.377107093945	-0.377563524308
0.28	-0.401981523992	-0.396561191409	-0.397063361275
0.27	-0.422218862039	-0.416085471513	-0.416637286099
0.26	-0.442608855635	-0.435682486906	-0.43628822072
0.25	-0.463162943151	-0.455354982954	-0.456019328174
0.24	-0.483893911366	-0.475105920429	-0.475834043663
0.23	-0.504816117176	-0.494938501893	-0.495736111163
0.22	-0.52594575696	-0.514856202585	-0.515729626872
0.21	-0.547301196487	-0.534862806803	-0.535819091168
0.2	-0.568903378502	-0.554962451052	-0.55600947122
0.19	-0.590776331066	-0.575159675629	-0.576306277142
0.18	-0.612947808168	-0.595459486795	-0.596715655503
0.17	-0.635450106273	-0.615867432404	-0.617244505392
0.16	-0.658321118293	-0.63638969484	-0.637900624192
0.15	-0.681605713159	-0.65703320652	-0.658692893096
0.14	-0.70535756993	-0.677805795243	-0.679631516695
0.13	-0.729641659303	-0.698716369708	-0.700728337591
0.12	-0.754537668314	-0.719775160117	-0.721997257325
0.11	-0.780144834994	-0.740994035942	-0.743454811816
0.1	-0.806588954046	-0.762386934521	-0.765120977703
0.09	-0.834032842384	-0.783970453459	-0.787020335355
0.08	-0.862692546163	-0.805764693429	-0.809183804454
0.07	-0.892863547668	-0.82779449947	-0.831651341943
0.06	-0.924965445281	-0.850091368297	-0.854476350203
0.05	-0.959623359768	-0.872696538483	-0.877733341688
0.04	-0.997829586606	-0.895666351782	-0.901532374787
0.03	-1.04130424881	-0.919082452184	-0.926049311281
0.02	-1.09344705552	-0.943073916731	-0.951599607994
0.01	-1.16262269606	-0.967876311495	-0.978866047942

VALIDITY OF THE APPROXIMATE SERIES SOLUTION TO THE SIMPLIFIED OZONE MODEL

1	1	1	1
0.98	0.963979803063	0.963979899328	0.96397980337
0.96	0.927877199061	0.927878575499	0.927877694124
0.94	0.891688824155	0.891694344921	0.891691845469
0.92	0.855411102333	0.855425452728	0.855420449548
0.9	0.819040227096	0.819070068151	0.819061618372
0.88	0.782572141121	0.782626279487	0.782613378363
0.86	0.746002513626	0.746092088609	0.746073664382
0.84	0.709326715114	0.709465404971	0.709440313189
0.82	0.67253978912	0.67274403904	0.672711056264
0.8	0.635636420533	0.6359256951	0.635883511915
0.78	0.598610899974	0.599007963331	0.598955176563
0.76	0.561457083617	0.561988311084	0.561923415121
0.74	0.52416834776	0.524864073247	0.524785450321
0.72	0.486737537261	0.487632441572	0.487538350862
0.7	0.44915690685	0.45029045282	0.450179018189
0.68	0.41141805408 1	0.41283497557	0.412704171727
0.66	0.373511842453	0.375262695475	0.375110332308
0.64	0.335428312917	0.337570098755	0.33739380353
0.62	0.297156581593	0.29975345363	0.299550650703
0.6	0.258684721025	0.261808789385	0.261576676974
0.58	0.219999621695	0.223731872653	0.223467396158
0.56	0.181086829696	0.185518180466	0.185218001672
0.54	0.141930355464	0.147162869474	0.146823330848
0.52	0.102512447131	0.10866074065	0.10827782375
0.5	0.0628133203298	0.0700061986089	0.0695754753658
0.48	0.0228108339819	0.031193204472	0.0307097798126
0.46	-0.0175199014632	-0.00778477904673	-0.00832633519436
0.44	-0.0582070009894	-0.0469348520182	-0.047540585832
0.42	-0.0992823904851	-0.0862647532629	-0.0869414234685
0.4	-0.140782531827	-0.125782950637	-0.126538150483
0.38	-0.182749329628	-0.16549874918	-0.166341044491
0.36	-0.22523127729	-0.20542242178	-0.206361532483
0.34	-0.268284922559	-0.245565368524	-0.246612388692
0.32	-0.311976766081	-0.285940313095	-0.28710798927
0.3	-0.356385756524	-0.326561547625	-0.327864633722
0.28	-0.40160662294	-0.367445241945	-0.368900958221
0.26	-0.447754406751	-0.408609839937	-0.410238475993
0.24	-0.494970753382	-0.450076575955	-0.451902297408
0.22	-0.543432855118	-0.491870160607	-0.493922110691
0.2	-0.593366513879	-0.534019711568	-0.536333551893
0.18	-0.645065841218	-0.576560049807	-0.579180176541
0.16	-0.698924116781	-0.619533560347	-0.622516399844
0.14	-0.75548439341	-0.662992963244	-0.666412074269
0.12	-0.815527317636	-0.707005630614	-0.710960006592
0.1	-0.880234878765	-0.751660707513	-0.756289166928
0.08	-0.951525966365	-0.797081768916	-0.802590060868
0.06	-1.03283993774	-0.843451746278	-0.850169827025
0.04	-1.13136083199	-0.891070032259	-0.899595723521
0.02	-1.26684762176	-0.940520899703	-0.952202050576

indicate that the contribution of the second order term is very small. This result indicates that the approximate solution with only first order term is a very good approximation to the simplified model. Also notice that this approximate solution (Eq.37) is sensitive only to the value of "a" and "bR", i.e. as long as "bR" remain constant, any combination of "b" and "R" can be used. This result can be observed graphically in figure (61). Notice in this figure that different combination of "b" and "R" will result in an identical outcome.

It is worthwhile to mention the dependency of the model on the absolute value of the concentration. Notice from the tables that both simulations were performed with identical HC/NO ratio but different values for the initial concentration of the primary pollutants. Comparison of the results indicate that the experiment with higher initial concentration (table X) ultimately resulted in a higher concentartion of ozone, but it will take longer to achieve this high concentration.

The second approach to justify the interdependency of "b" and "R" can be achieved by analyzing the result of our analytical equation (Eq.28). This equation can be expressed in terms of Z where Z = m/kd.

$$[No\text{-}O_3] = [No\text{-}O_3]_o [HC]^{\frac{1}{z+1}} [HC]_o^{\frac{1}{z+1}} + \frac{z}{z+1}[HC]^{\frac{1}{z+1}} \left\{ \frac{z+1}{z}\left[HC^{\frac{z}{z+1}} - HC_o^{\frac{z}{z+1}}\right]\left(a + \frac{bR}{R-1}\right) - \left(\frac{bR}{R-1}[HC]_o^{\frac{-z(R-1)}{z+1}}\right)\left[HC^{\frac{zR}{z+1}} - HC_o^{\frac{zR}{z+1}}\right]\left[\frac{z+1}{zR}\right]\right\} \qquad (39)$$

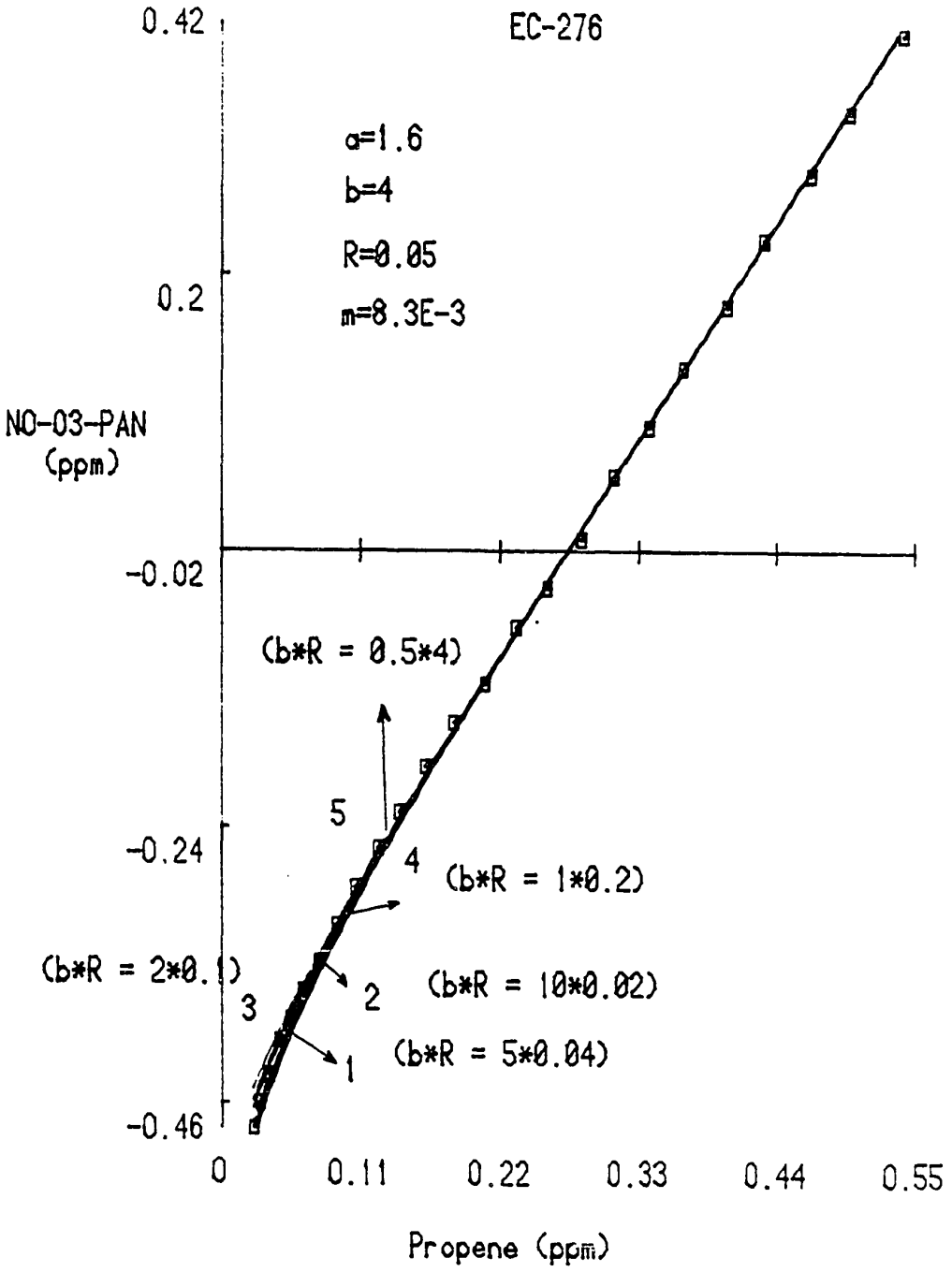


Figure 61. Model's sensitivity toward "b" and "R".

In the limit where $z \rightarrow \infty$ this equation will reduce to

$$[NO\text{-}O3] = [NO\text{-}O3]_o + [HC\text{-}HC]_o(a+bR/R-1) - b[HC]_o/(R-1)\{(HC/HC)_o^R - 1\} \quad (40)$$

Also, it was observed that as hydrocarbon reactivity increases, the model predicts smaller value for "R", i.e.,

$$\lim_{z \rightarrow \infty} R-1 \simeq -1$$

Under this condition Eq. (40) will be reduced to

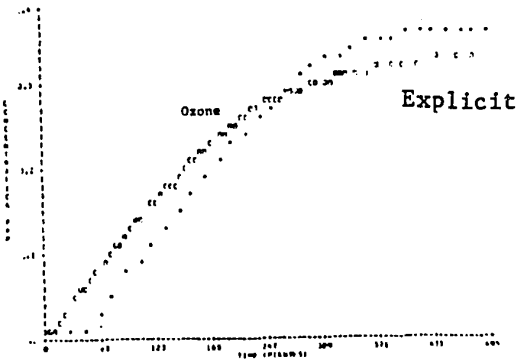
$$[NO\text{-}O3] = [NO\text{-}O3]_o + [HC\text{-}HC]_o(a-bR) \quad (41)$$

This equation also explicitly demonstrates the interdependecy of "b" and "R". Notice that for a reactive hydrocarbon the NO photooxidation model can be represented by a linear equation with the magnitude of its slope dependent upon "a" and "bR".

i- n-Butane/NOx

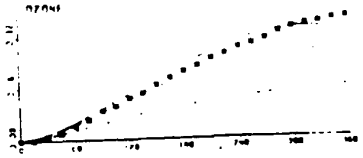
Comparison of the results of our simplified approach to some of the available explicit mechanisms for n-Butane/NOx (42,60,81) are presented in figures (62,67-68). Since in some cases only very limited simulation results are available (42) we will limit our comparison to the available reported data.

In Fig (62) the results of a computer simulation for EC-178 is presented. Notice that Hendry et al explicit mechanism (60) overpredicts the ozone profile up to 250 minutes and then underpredicts for the rest of the experiment. The carter et al explicit mechanism (42) will mimic the behavior of the experimental data with slight overprediction up to 300 minutes. (In this figure the upper curve is the result of the explicit model and the two curves below are the result of the sensitivity of their model toward the reaction of HO2+NO). This model would underpredict the ozone concentration if they extended the simulation result to the full 495 minutes for which the experiment was run (76). The explicit mechanism proposed by Whitten et al (81) reasonably well reproduces the behavior of the experimental data. Notice that the simplified model is able to reproduce the ozone profile reasonably well for most part of the experiment with some overprediction toward the end of the

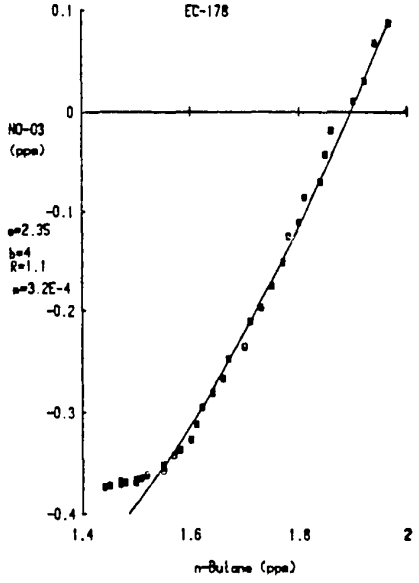


Explicit Model

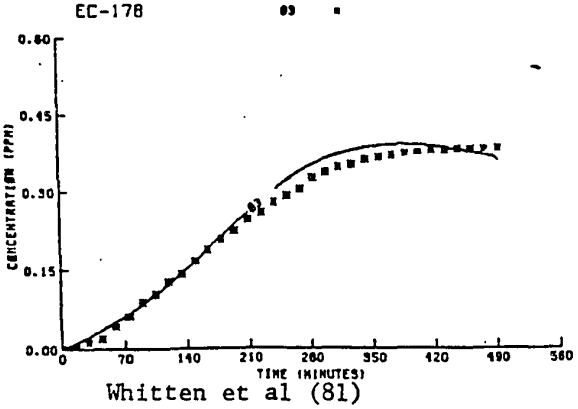
Hendry et al (60)



Carter et al (42)



Simplified Model



Whitten et al (81)

Figure 62. Comparison of the simplified model prediction with the explicit model for n-Butane/NOx EC-178

ozone accumulation region. This overprediction as noticed earlier is due to lack of provision for ozone removal paths. The most important removal paths for ozone include reactions such as ozone photolysis, reaction of ozone with NO2, and ozone wall loss. These reactions were left out from the NO photooxidation model simply because the contribution of these reactions in the NO-photooxidation regime are very small. But once NO is depleted, i.e, NO2 and ozone reach appreciable concentration these ozone removal paths become significant and their contribution for an accurate prediction of ozone concentration must be considered.

To examine the effect of these removal paths in suppressing the ozone concentration we integrated numerically the detailed mechanism for the n-Butane/NOx system provided by Whitten et al (45) with the CHEMK program. We performed computer simulations with the initial condition similar to EC-178 (76). In the first experiment all reactions as were proposed by Whitten et al were included (45). The result of such a simulation is presented in Fig. (63). Notice that the simplified model (solid line) also overpredicts the simulated data (Squares) obtained from CHEMK.

In the following computer simulations for simplicity we set the dilution rate constant equal to zero and systematically investigate the effect of each competing removal path for the removal of ozone seperately. To observe the effect of ozone photolysis we set its rate constant equal to

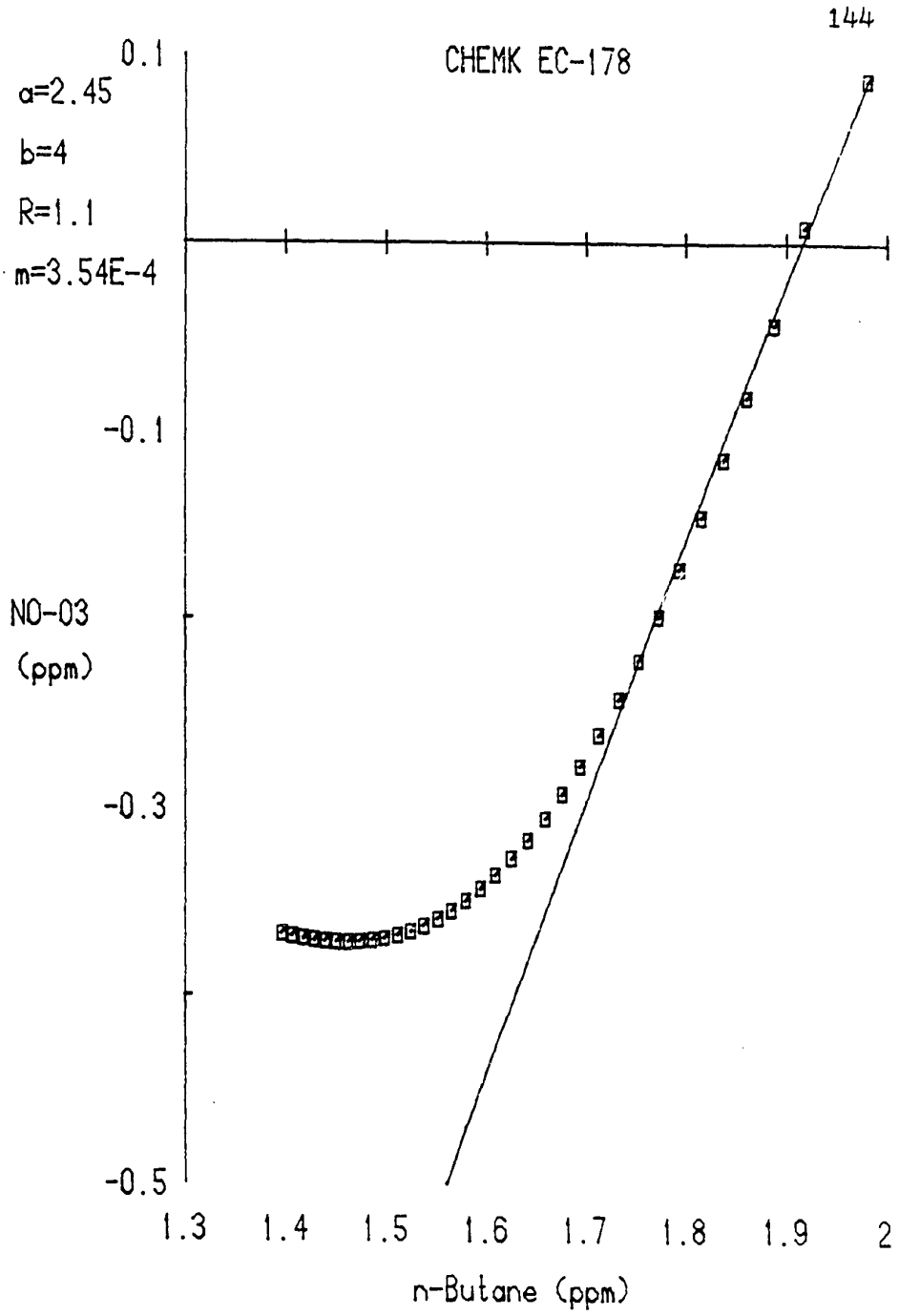


Figure 63. CHEMK computer simulation for EC-178.

zero. Removal of ozone photolysis from the detailed mechanism resulted in higher prediction of ozone concentration, Fig (64).

In the next simulation, the rate constant of the reaction of NO2+O3 also was set equal to zero. Removal of this reaction resulted in still higher ozone concentration Fig (65). In the last simulation ozone wall loss was set equal to zero, Fig (66). Notice that by eliminating these ozone removal paths from the detailed mechanism, the prediction of the simplified model is in very good agreement with the calculated parameters from the explicit mechanism. These experiments demonstrate the fact that for an accurate prediction of ozone concentration in the ozone accumulation regime (where NO2 and ozone reach appreciable concentration) ozone removal paths must be treated explicitly.

In figure (67) the results of simulations for EC-162 are presented. In this figure computer simulation results for the Hendry et al explicit mechanism, Whitten et al explicit mechanism and our simplified model are presented. No data was available for Carter et al (42). The same trend was observed, i.e., Hendry et al overpredicts the ozone profile while Whitten et al reasonably well reproduces the ozone curve for the most part of the experiment and overpredicts the ozone concentration toward the end of the experiment. The simplified model is in good agreement with the behavior of the experimental data. One more example for the n-Butane/NOx result for Whitten et al and our model is

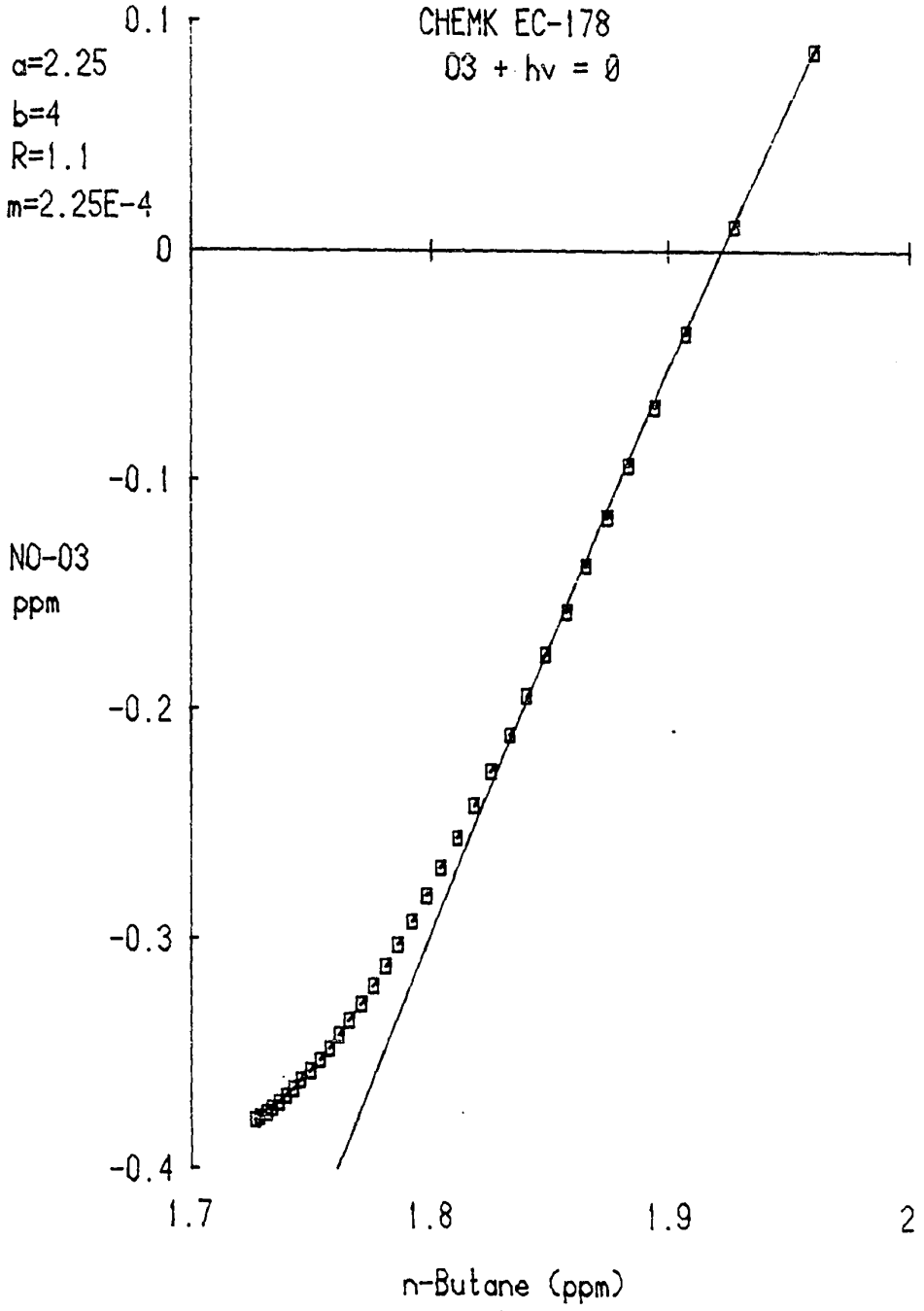


Figure 64. Effect of ozone photolysis on CHEMK simulated data.

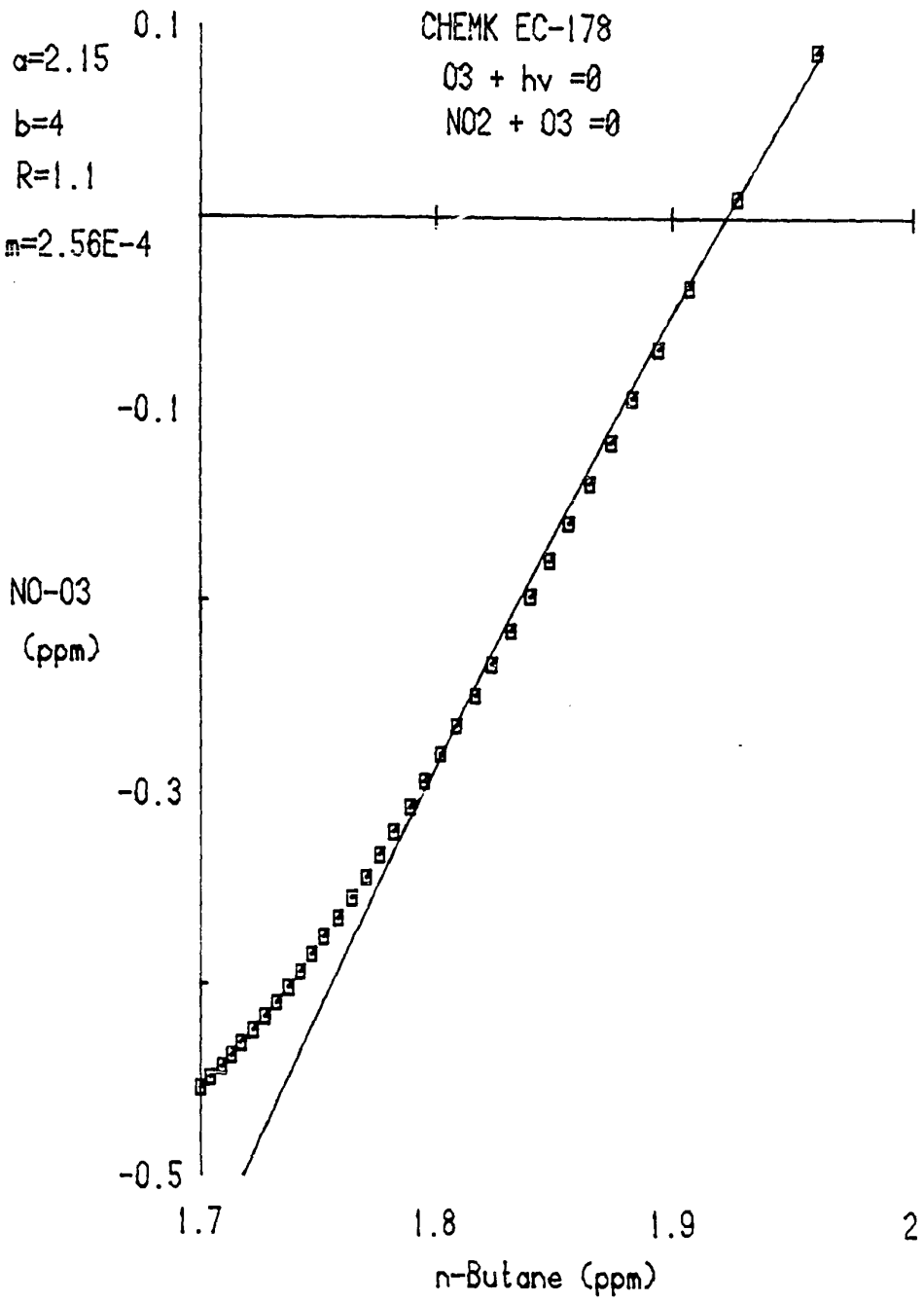


Figure 65. Effect of ozone photolysis and NO_2+O3 on the CHEMK simulated data for EC-178.

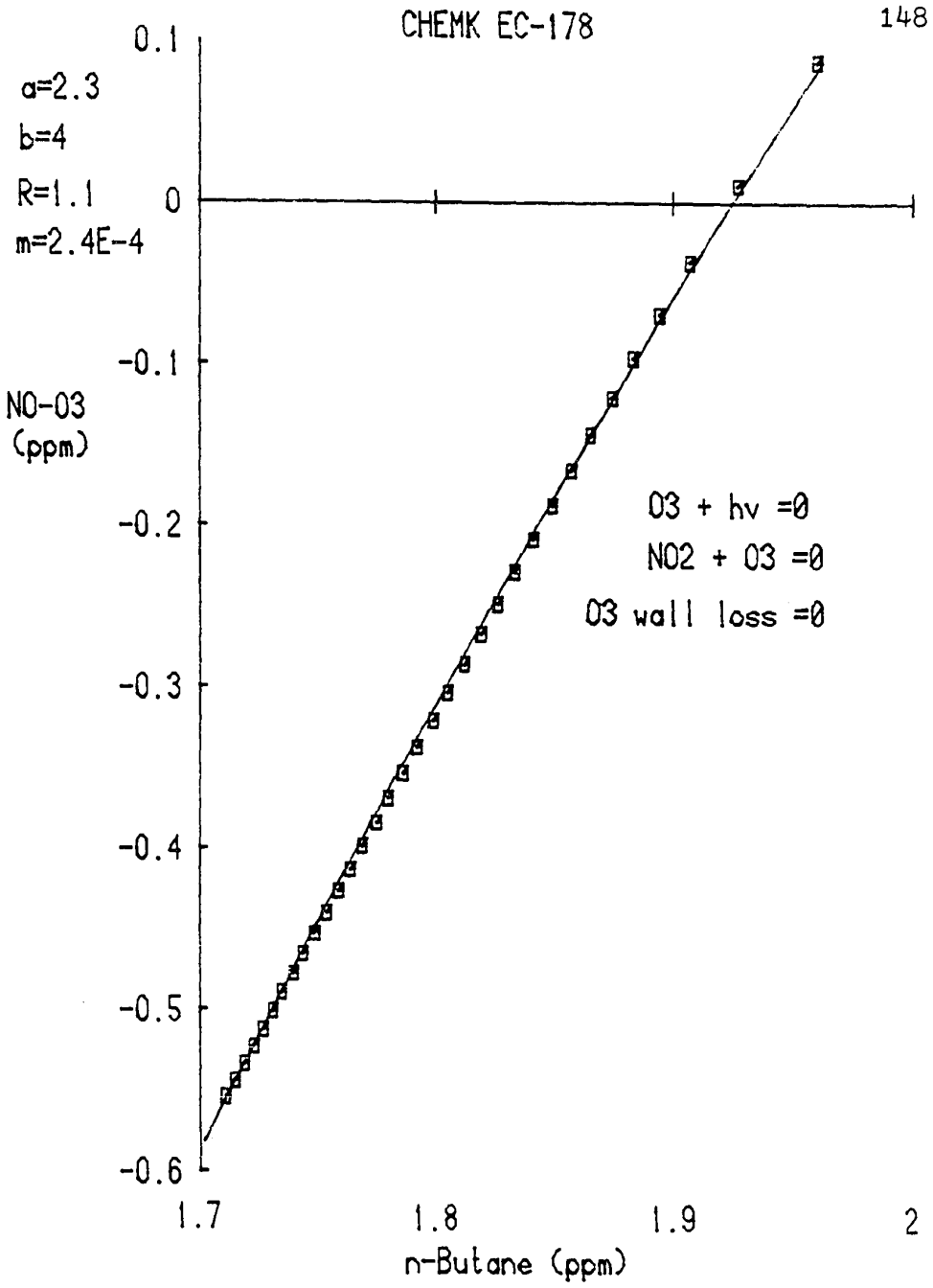
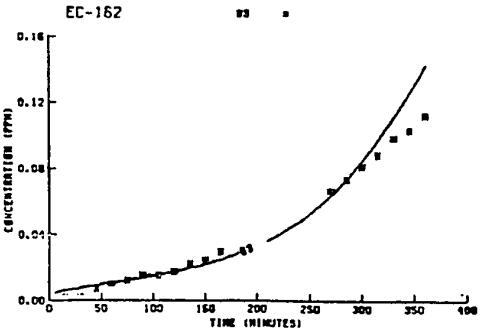
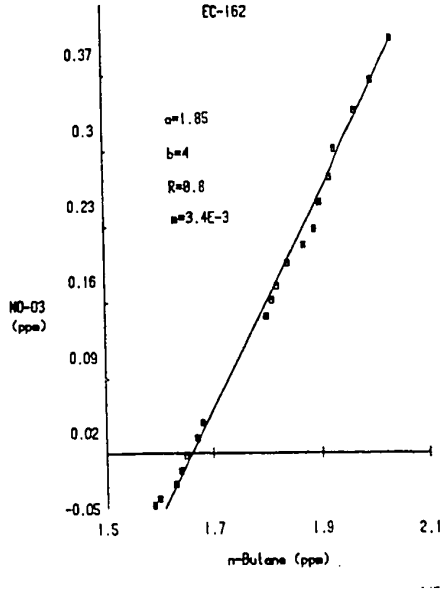


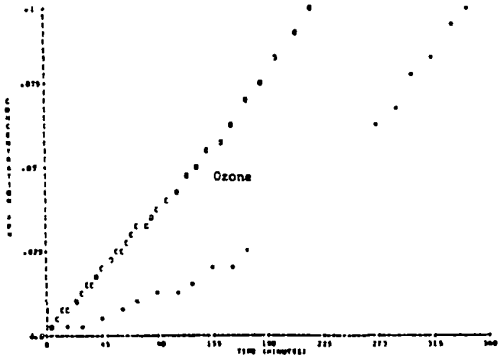
Figure 66. Effect of ozone photolysis, NO_2+O3 and ozone wall loss on the CHEMK simulated data for EC-178.



Whitten et al (81)



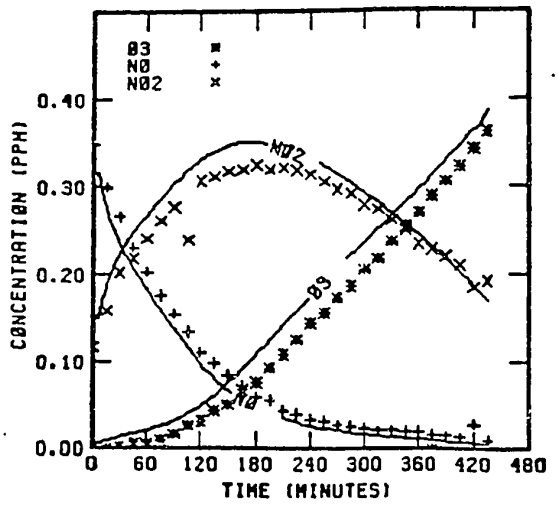
Simplified Model



Hendry et al (60)

Figure 67. Simplified model vs. explicit for EC-162

presented in Fig (68). No data are available for Carter et al and Hendry et al.



Whitten et al (81)

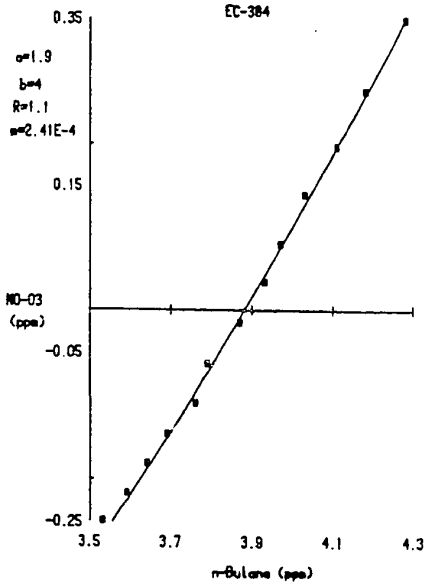
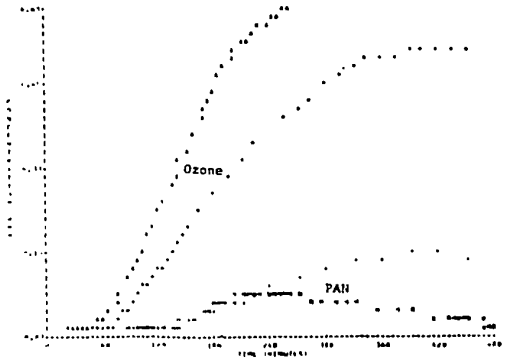
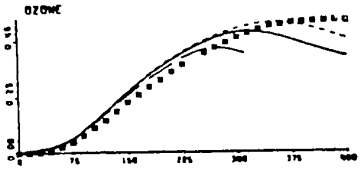


Figure 68. Comparison of the simplified model with the explicit mechanisms for EC-304

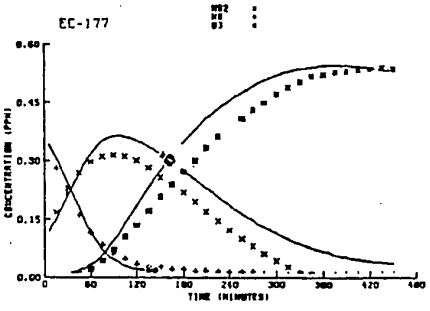
The result of computer simulation for EC-177 is presented in Fig (69). Notice that Hendry et al explicit mechanism (60) again will overpredict the ozone profile, while Carter et al (42) after 360 minutes underpredict the ozone concentration. Also notice that in order to compensate for ozone underprediction Carter et al reduced the value of the rate constant for the reaction of N2O5 + H2O, i.e., reducing the sink for ozone. The model's sensitivity toward the variation of the rate constant of N2O5+H2O is presented in this figure. The middle curve corresponds to the standard model calculation (42). When this value was increased by about a factor of four or set to zero the lower or upper curves were obtained respectively.
For the same experiment, Whitten et al overpredict the ozone concentration up to 360 minutes. Notice that the NO2 profile is also overpredicted. The reported PAN curve by the same modelers (81) also underpredicts tha PAN profile which suggests that the chemistry of PAN ($RO_2+NO_2 \rightleftharpoons PAN$) is not treated properly. The simplified model can reasonably well predict the behavior of the ozone profile.
In Figure (70) the result of computer simulation for EC-216 is presented. In this figure the updated mechanism for HC/NOx systems by Atkinson et al (54) is presented. Notice that for this experiment all explicit models overpredict the ozone concentration. Two more examples for the propene/NOx



Hendry et al (60)



Carter et al (42)



Whitten et al (81)

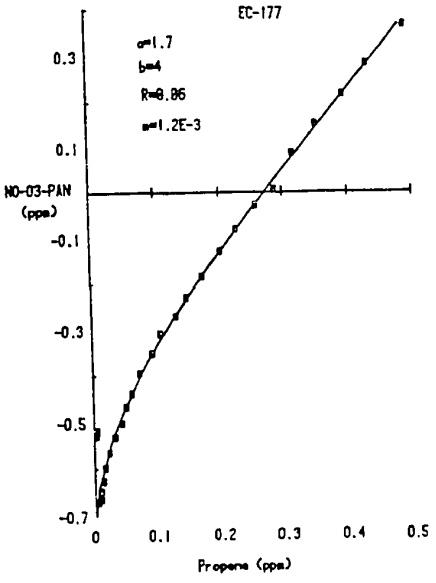
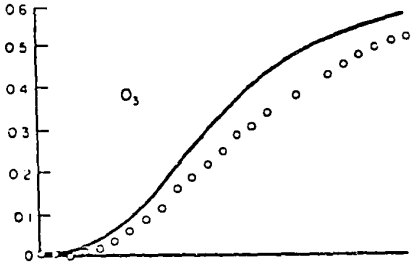
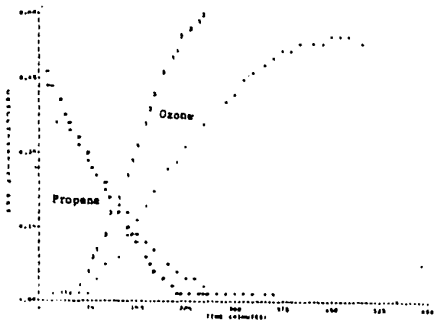


Figure 69. Comparison of the Simplified Model with the Explicit mechanisms for Propene/NOx EC-177



Atkinson et al (54)



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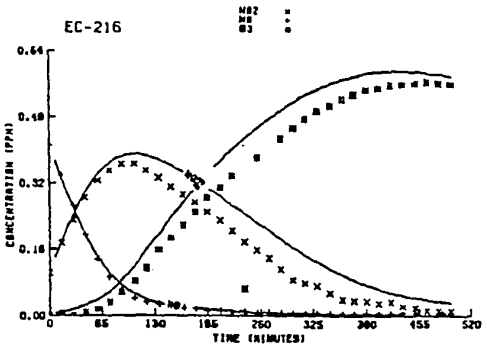

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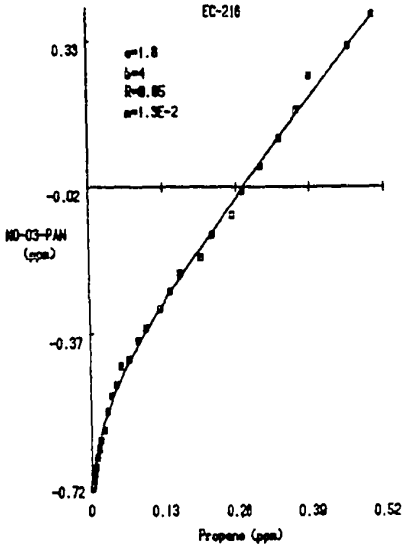
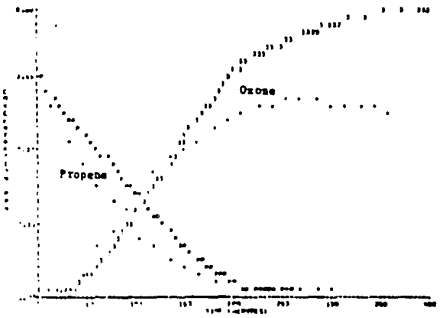


Figure (70) Simplified model vs. explicit mechanisms for EC-216

system are presented in Figures (71-72).



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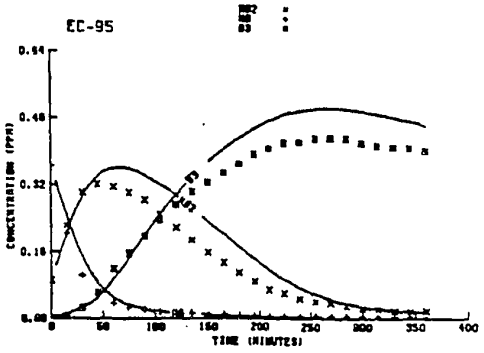


Whitten et al (81)

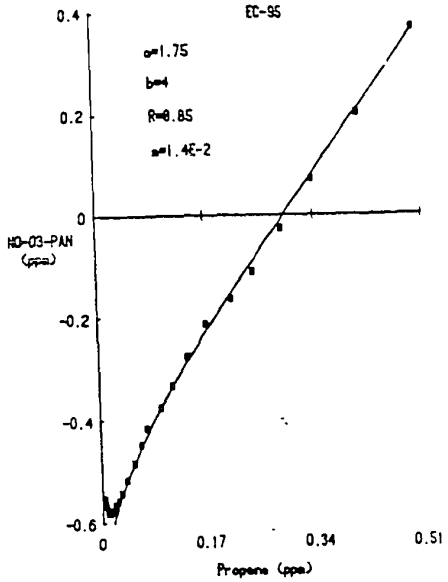
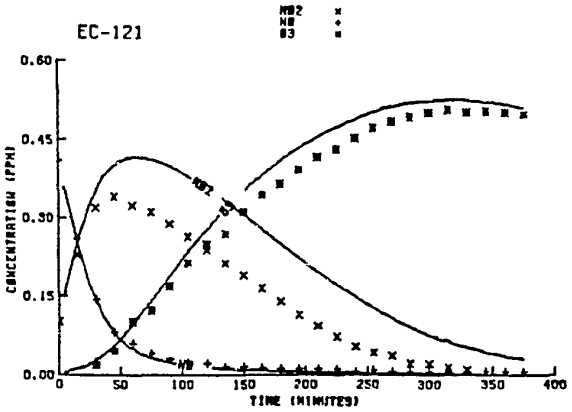
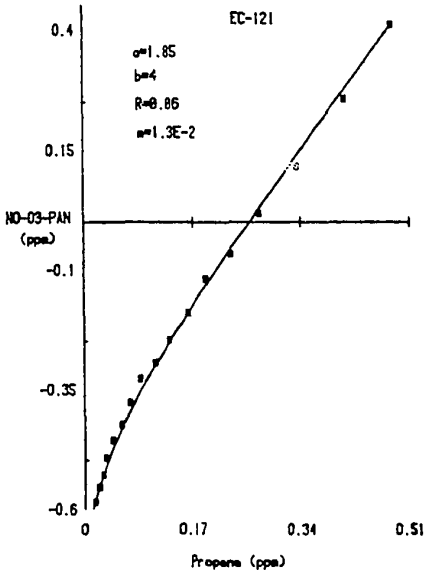


Figure 71. Simplified Model vs. Explicit mechanisms for EC-95



Whitten et al (81)



Simplified Model

Hendry et al (60)

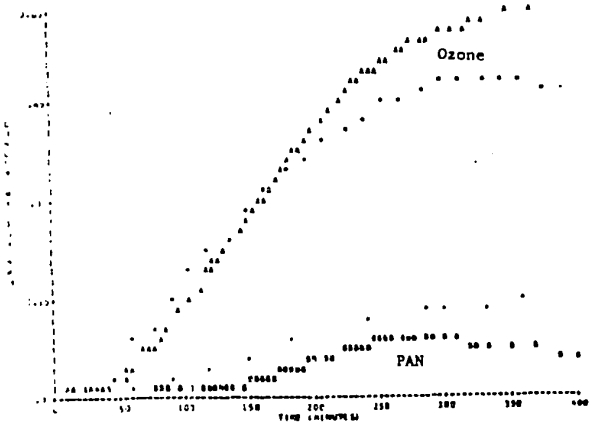


Figure 72. Simplified Model vs. Explicit Models for EC-121

VII-c Summary of Results and Conclusion

A greatly simplified photochemical ozone model which accurately describes the relationship of photochemical ozone formation to precursor hydrocarbons and oxide of nitrogens is developed. This model met its prime objective to eliminate the need for the "brute force" approach (traditional approach) to integrate tens or even hundereds systems of simultaneous differential equations. We have sought to develop the full kinetic potential for simplification which this chemical system may have. By design, the mechanism takes advantage of common features of hydrocarbon and free radical reactions to minimize the required number of species, while retaining a high degree of detail and certain elements of chemical realism. This model uses a bare minimum number of chemical reactions to describe the ozone-forming potential of a single hydrocarbon and its oxidation products with only three rate parameters. The model results in a single differential equation for each hydrocarbon. This differential equation is solved explicitly for low NOx concentration. For the reactive hydrocarbons the model is sensitive to only two effective rate parameters, "a" and "bR".

The simplified model is tested against available smog chamber data (75-76) and reproduces the ozone curve quite well, while yielding rate parameters for propene and n-Butane in good agreement with the explicit mechanisms

(42,45,81). The simplified model predicts 10% lower value for "a", suggesting that some portion of RO2 which reacts with NO forms nitrates (RNO3) rather than ozone. This result is in agreement with recent experimental observations by Atkinson et al (82). When the model is extended past the NO photooxidation regime and into the ozone accumulation regime, termination reactions must be included. Also, the ozone/propene reaction distorts the shape of the time-independent curve, resulting in less ozone production and lower effective values of the rate parameters.

VII-d Expected Benefits

It is worthwhile to mention some unique features of the simplified ozone model. Briefly they are:

1. Change in atmospheric hydrocarbon composition due to controls, alternate fuels, etc. may be directly assessed.

2. Ambient OH measurements may be used as input to the model giving the greatest confidence in the output.

3. Both short and long range transport will be simulated with the same model.

4. The model will be easy and inexpensive to run from the standpoint of chemistry at least and could be coupled with a very complex site specific dispersion model at little increase in complexity to that of the dispersion model. Finally, this model can easily be applied in a very straightforward manner to the experimental data and the rate

parameters responsible for the rate of NO photooxidation which ultimately controls the ozone concentration can be readily obtained from time independent analysis of the experimental data.

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GC/NO_x/Rockwell Aim-65 Basic program

```
5 PRINT"INPUT TIME OF COMPLETE CYCLE":INPUT QV
10 PRINT"INPUT TIME FOR CHRO-MATOGRAM IN MIN.":INPUTA2
12 PRINT"INPUT NOX-NO SAMPLE TIME":INPUTZ2
13 PRINT"TIME G.C. OVEN DOOR OPEN AFTER INJ":INPUTZ3
15 PRINT"INPUT AREA REJECT   10*X (INPUT X)":INPUTA3
20 PRINT"INPUT THE SLOPE SET-TING":INPUTS
25 PRINT"WHEN READY INPUT 1":INPUTK
26 DIMPA(20),RT(20),DG(20),SL(5)
30 P=3
40 POKE4,32:POKE5,13:X=USR(W):POKE3337,P
41 POKE4,185:POKE5,13:X=USR(W):POKE4,142:POKE5,13
47 B=224
51 RN=RN+1:PRINT!"RUN#";RN
52 NB=0:GOSUB400
53 E=PEEK(40962)
54 A=EDRB:POKE40962,A
56 POKE40960,63
57 POKE40972,220:X=USR(W):FORM=1TO25:NB=NB+USR(W):NEXT
58 GOSUB600:IFZ2=.75=>TTHEN58
59 NB=NB/25:X=USR(W):Z5=USR(W):POKE40960,191:IFRN=1THENPZ=Z5
60 PRINT!"NB=";:Q1=NB/P:GOSUB700:PRINT!"NO=";:Q1=(Z5-NB)/P:GOSUB700
61 GOSUB600:IFZ2=>TTHEN61
62 X=USR(W):Z5=USR(W):PRINT!,"NOX=";:Q1=(Z5-NB)/P
63 GOSUB700:POKE40960,223
64 GOSUB600:IFZ2+Z3=>TTHEN64
65 POKE40972,255
66 FORI=0TO5:DG(I)=USR(W)/P:NEXT:GOSUB600
67 FORJ=1TO20:S1=S
68 T2=T:DG(6)=USR(W)/P:S0=SU:GOSUB600
69 IFABS(S0)<ABS(S1)THENS1=S0
70 IFA2+Z2<=TTHEN191
72 FORI=0TO5:DG(I)=DG(I+1):NEXT
73 SU=0:FORI=1TO5:N=I-3
75 SU=SU+DG(I)*N:NEXT:SU=SU*.06/P
76 S1=0
95 IFSU>SORC2=1THEN105
100 C3=0:GOTO68
105 C3=C3+1:IFC3=1THENPA(J)=0:GOTO120
110 IFC6>5ANDSU-S2>STHEN193
112 C8=0
115 GOTO125
120 S2=S1:PA(J)=DG(3):P2=DG(3):GOTO68
125 PA(J)=PA(J)+DG(3):IFC3<5THEN68
130 C2=1:IFSU-S2<SANDC6<5THENC4=C4-1:GOTO140
133 IFC6>4THEN150
134 C6=0
135 C4=C3:GOTO68
140 IFC4=0THENC3=0:C6=0:C7=0:C4=0:C2=0:GOTO68
150 IFS2-SU>STHENC6=C6+1:GOTO160
152 IF-SU+S2<STHENC7=C7+1:GOTO165
155 C7=0:GOTO68
160 IFC6=1THENRT(J)=T:GOTO68
165 IFC7<10THEN68
170 IFSP>0THEN200
175 PA(J)=(PA(J)-(P2+DG(3))/2*C3)*(T-T2)
180 C2=S:C3=0:C6=0:C7=0:SP=0
185 IFPA(J)<10*A3THEN68
190 NEXT
191 IFSP>0THENLV=1:GOTO200
192 GOTO220
193 C8=C8+1:IFC8=5THENC8=0:GOTO195
194 GOTO125
195 SP=SP+1:SL(SP)=C3:C6=0:C7=C6:NEXT
```

```
200 PB=(DG(3)-P2)/C3
202 L=SP:SP=SP+1:SL(SP)=C3
205 FORI=JTOJ-LSTEP-1
210 PC=(PB/2*(SL(SP)+SL(SP+1))+P2)
211 PA(I)=(PA(I)-PC*(SL(SP)-SL(SP-1)))*(T-T2)
212 SP=SP-1:NEXTI
213 C7=0:C6=0:C3=0
215 C2=0:SP=0:IFLV=1THENLV=0:GOTO220
217 GOTO190
220 IFJ=1THENPRINT!"NO PEAK":GOTO255
225 SM=0:FORK=1TOJ-1:SM=SM+PA(K):NEXTK
226 PRINT!" "
227 PRINT!"  #    RT    P    %A"
230 FORK=1TOJ-1:Z=PA(K)/SM*100
235 PRINT!K;
240 W=2:Q1=RT(K)-Z2:GOSUB700:Q1=PA(K):W=2:GOSUB700
245 Q1=Z:GOSUB700
247 PRINT!" "
250 NEXT:PRINT!,"END OF RUN"
255 POKE40972,223
256 GOSUB600:IFT<QVTHEN256
257 GOTO51
400 POKE3334,0:POKE3333,0:POKE3332,0:RETURN
600 T=(PEEK(3332)*255+PEEK(3333)+PEEK(3345)/20)/60
605 RETURN
700 PRINT!INT(Q1*10^W+.5)/10^W;
710 W=0:RETURN
1000 POKE40960,191
1001 X=USR(W)/P:PRINTX:GOTO1001
2000 POKE40960,255
2001 X=USR(W)/P:PRINTX:GOTO2001
```

APPENDIX B

CHEMK DOCUMENTATION

CHEMK is a Fortran based computer program which once given a kinetic mechanism, computes the concentration-time profile of the various species. This program initially was written by Whitten G.Z. and incorporates the Gear numerical integration technique package of Hindmarsh (77). This version has been modified such that in addition to concentration-time profile, rate of the elementary reactions in descending order of significance and also, net rate of reaction for a given species will be computed. Also this modified version uses the optimized values for "initial guess" and "error limit". These two parameters set the starting point for stiff numerical integration and error bound for achievement of the convergence test criteria respectively. The optimized parameters resulted in drastic reduction in the computation time (CPU).

Most CHEMK subroutines remained unchanged as they were proposed except the subroutines called Rate, Yfix and Main. A copy of these routines are presented in tables (XI-XIII). All subroutines are converted from ASCII to machine level

TABLE XI

CHEMK "ARATE" SUBROUTINE

```
1000      SUBROUTINE ARATE (RT)
1010C**************************************************************************
1020C                                                                          *
1030C  ROUTINE NAME: ARATE                                                     *
1040C                                                                          *
1050C  PURPOSE: COMPUTE ACTUAL RATES FOR THE REACTIONS INVOLVING               *
1060C           SPECIFIC SPECIES.                                              *
1070C                                                                          *
1080C  INPUTS:                                                                *
1090C    PARAMETER INPUTS:                                                     *
1100C      RT                                                                  *
1110C                                                                          *
1120C    COMMON INPUTS:                                                        *
1130C                                                                          *
1140C  OUTPUTS:                                                               *
1150C    PARAMETER OUTPUTS:                                                    *
1160C                                                                          *
1170C    COMMON OUTPUTS:                                                       *
1180C                                                                          *
1190C  ROUTINES CALLED: NONE                                                   *
1200C                                                                          *
1210C                                                                          *
1220C**************************************************************************
1230C
1240C
1250      DIMENSION RT(200),ACRATE(200),NRN(200)
1260      DIMENSION SFACT(200),SRATE(200),KLIST(30)
1270C
1280      COMMON /ARXN/ ARS(200,7)
1290      COMMON /DATA/ NR,     KR(200,7), A(200), S(200),  RTITLE(7),
1300     &              TEMP,   ERR,
1310     &              TSTART,  TSTOP,            PC,      NP,
1320     &              SIG(102),IP(102),    ITYPE(200),     R(200),
1330     &              BK,     SG,                        DILUT
1340      COMMON /INOUT/ IN,IOUT,ITAPE,I4051,IECHO,ITCS,NTIN,NTWR
1350      COMMON /ASPEN/ NO, ASPEC(102)
1360      COMMON /CONST/ ISPAN, CHOLD(102), CHAR, NK(102), CC(102)
1370      COMMON /RLIST/ NLR(15), LIST(15,200), NUM, STITLE(15,15)
1380      COMMON /STOR/ PA(102)
1382C     DATA ITEK/33/
1390C
1400C
1410C
1420      IF(NO.EQ.999) GO TO 120
1430      WRITE (IOUT,90)
1440 90   FORMAT ('0THE NET RATES OF THE REACTIONS INVOLVING A GIVEN ',
1450     &        'SPECIES ARE:')
1460      DO 5 I=1,NO
1470         WRITE (IOUT,91) ASPEC(I)
1480 91      FORMAT ('0',A4)
1490         L=0
1500         DO 10 J=1,NR
1510            K=0
1520 20         K=K+1
1530            IF(ARS(J,K).NE.ASPEC(I)) GO TO 21
1540            KRC=KR(J,K)
1550            IF(L.EQ.0) GO TO 25
1560            JCHK=IABS(NRN(L))
```

TABLE XI

(continued)

```
1570            IF(JCHK.NE.J) GO TO 25
1580            IF((K.LE.3).AND.NRN(L).LT.0) SFACT(L)=2.
1590            IF((K.GT.3).AND.NRN(L).GE.0) SFACT(L)=2.
1600            IF((K.GT.3).AND.NRN(L).LT.0) SFACT(L)=0.
1610            GO TO 21
1620 25         L=L+1
1630            ACRATE(L)=RT(J)
1640            SFACT(L)=1.
1650            NRN(L)=J
1660            IF(K.LE.3) NRN(L)=-J
1670 21         IF(K.NE.7) GO TO 20
1680 10       CONTINUE
1690          DO 35 NIN=1,L
1700             ACRATE(NIN)=ACRATE(NIN)*SFACT(NIN)
1710 35       CONTINUE
1720C
1730C    INCLUDE RATE OF DILUTION FOR THE SPECIES
1740C
1750          IF(DILUT.EQ.0.) GO TO 150
1760          L=L+1
1770          ACRATE(L)=DILUT*PA(KRC)
1780          SFACT(L)=1.
1790          NRN(L)=-99999
1800C
1810C    PUT THE RATES IN DESCENDING ORDER
1820C
1830 150      IF(L.LE.1) GO TO 93
1840 31       NOTE=0
1850          DO 30 M=1,L-1
1860             IF(ACRATE(M).GE.ACRATE(M+1)) GO TO 30
1870             BUFF=ACRATE(M)
1880             IBUFF=NRN(M)
1890             ACRATE(M)=ACRATE(M+1)
1900             NRN(M)=NRN(M+1)
1910             ACRATE(M+1)=BUFF
1920             NRN(M+1)=IBUFF
1930             NOTE=NOTE+1
1940 30       CONTINUE
1950          IF(NOTE.NE.0) GO TO 31
1960C
1970C    DETERMINE THE SIGN OF THE REACTION
1980C
1990 93       IF(NRN(1).GE.0) GO TO 80
2000          NRN(1)=-NRN(1)
2010          ACRATE(1)=-ACRATE(1)
2020 80       ASUM=ACRATE(1)
2030          DO 85 M=1,L-1
2040             IF(NRN(M+1).GE.0) GO TO 87
2050             NRN(M+1)=-NRN(M+1)
2060             ACRATE(M+1)=-ACRATE(M+1)
2070 87          ASUM=ASUM+ACRATE(M+1)
2080 85       CONTINUE
2090C
2100C    WRITE OUT THE RATES FOR EACH SPECIES
2110C
2120          IF(ISPAN.NE.0) GO TO 95
2130          WRITE (IOUT,96) (NRN(N), ACRATE(N),N=1,L)
2133C           WRITE(ITEK,96) (NRN(N),ACRATE(N),N=1,L)
```

TABLE XI

(continued)

```
2140 96      FORMAT ((2X,8(1X,I3,':',1PE10.3,1X)))
2150         GO TO 97
2160 95      WRITE(IOUT,92) (NRN(N), ACRATE(N), N=1,L)
2163C           WRITE(ITEK,92) (NRN(N),ACRATE(N),N=1,L)
2170 92      FORMAT ((2X,4(1X,I2,':',1PE10.3,2X)))
2180C
2190C   WRITE OUT THE SUM
2200C
2210 97      WRITE (IOUT,81) ASUM
2220 81      FORMAT ('  SUM:',1PE10.3)
2230 5     CONTINUE
2240 94    FORMAT ('0')
2250C
2260C   ORDER SELECTED REACTION RATES
2270C
2280 120   IF(NUM.EQ.0) GO TO 110
2290       DO 50 I=1,NUM
2300          NMR=NLR(I)
2310          N=0
2320          K=0
2330 102      N=N+1
2340 112      K=K+1
2350          SRATE(K)=RT(IABS(LIST(I,N)))
2360          KLIST(K)=LIST(I,N)
2370          IF(N.EQ.1) GO TO 111
2380          IF(IABS(LIST(I,N)).NE.(IABS(LIST(I,N-1)))) GO TO 111
2390          N=N-1
2400          K=K-1
2410 111      IF(IABS(LIST(I,N)).NE.(IABS(LIST(I,N+1)))) GO TO 101
2420          SRATE(K)=SRATE(K)+RT(IABS(LIST(I,N)))
2430          N=N+1
2440          NMR=NMR-1
2450          IF(N.GE.NLR(I).AND.K.NE.NMR) GO TO 112
2460 101      IF(N.LT.NLR(I)) GO TO 102
2470C
2480C   PUT IN DESCENDING ORDER
2490C
2500          IF(NMR.LE.1) GO TO 103
2510 104      NOTE=0
2520          DO 105 M=1,NMR-1
2530             IF(SRATE(M).GE.SRATE(M+1)) GO TO 105
2540             BUFF=SRATE(M)
2550             IBUFF=KLIST(M)
2560             SRATE(M)=SRATE(M+1)
2570             KLIST(M)=KLIST(M+1)
2580             SRATE(M+1)=BUFF
2590             KLIST(M+1)=IBUFF
2600             NOTE=NOTE+1
2610 105      CONTINUE
2620          IF(NOTE.NE.0) GO TO 104
2630C
2640C   DETERMINE THE SIGN OF THE REACTION
2650C
2660 103      DO 106 M=1,NMR
2670             IF(KLIST(M).GE.0) GO TO 106
2680             KLIST(M)=-KLIST(M)
2690             SRATE(M)=-SRATE(M)
2700 106      CONTINUE
2710          WRITE (IOUT,98) (STITLE(I,L),L=1,15)
2720 98      FORMAT ('0',15A4)
2730          ASUM=SRATE(1)
2740          DO 108 M=1,NMR-1
2750             ASUM=ASUM+SRATE(M+1)
2760 108      CONTINUE
```

TABLE XI

(continued)

```
2770          IF(ISPAN.NE.0)GO TO 107
2780          WRITE (IOUT,96) (KLIST(N),SRATE(N),N=1,NMR)
2790          GO TO 109
2800 107      WRITE (IOUT,92) (KLIST(N), SRATE(N), N=1,NMR)
2810 109      WRITE (IOUT,81) ASUM
2820 50    CONTINUE
2830 110   WRITE (IOUT,94)
2840       RETURN
2850       END
```

TABLE XII

CHEMK "YFIX" SUBROUTINE

```
      SUBROUTINE YFIX (NO,TLAST,C,NQ,INDEX)
C*****************************************************************************
C                                                                              *
C  ROUTINE NAME: YFIX                                                          *
C                                                                              *
C  PURPOSE: THIS IS THE NORMAL OUTPUT ROUTINE                                  *
C                                                                              *
C  INPUTS:                                                                     *
C    PARAMETER INPUTS:                                                         *
C      NO                                                                      *
C      TLAST                                                                   *
C      C(102,6)                                                                *
C      NQ  ITERATIONS BETWEEN SPOT CHECKS; SET TO 10000 IN MAINLINE            *
C      INDEX  FIRST TIME FLAG. DETERMINES IF YFIX HAS BEEN ENTERED             *
C             BEFORE. INITIALIZATION TAKES PLACE ON FIRST ENTRY.               *
C                                                                              *
C    COMMON INPUTS:                                                            *
C      /NAMES/ NS                                                              *
C              SPECIS(102)                                                     *
C      /DATA/ TSTOP                                                            *
C             RTITLE(7)                                                        *
C             ERR                                                              *
C             PC                                                               *
C             NR                                                               *
C             TSTART                                                           *
C      /STCOM1/ T                                                              *
C               H  TIME STEP SIZE                                              *
C      /STCOM2/ YMAX(102)                                                      *
C      /MODE/ KOUT                                                             *
C      /CHANGE/ NFLG                                                           *
C      /CONST/ ISPAN                                                           *
C              CHAR  HOLLERITH H                                               *
C                                                                              *
C  OUTPUTS:                                                                    *
C    PARAMETER OUTPUTS:                                                        *
C      INDEX                                                                   *
C                                                                              *
C    COMMON OUTPUTS:                                                           *
C      /STOR/ PA(102)                                                          *
C      /ASPEN/ NO                                                              *
C      /FRPLOT/ SAVTIM(80)                                                     *
C               NT                                                             *
C                                                                              *
C  ROUTINES CALLED: CLEAN                                                      *
C                   DIFFUN                                                     *
C                   ARATE                                                      *
C                                                                              *
C  LOCAL VARIABLES:                                                            *
C    C(102,6)                                                                  *
C    CH(102)                                                                   *
C    I    LOOP INDEX                                                           *
C    MS                                                                        *
C    MT                                                                        *
C    NHS                                                                       *
C    NN                                                                        *
C    NPLOT                                                                     *
C    NTP                                                                       *
C    TIME  HOLLERITH CONSTANT USED TO PRINT HEADER ON 4051 OUTPUT              *
C    THULT                                                                     *
C    TOLD                                                                      *
C    TPRINT                                                                    *
C    TSTEP                                                                     *
C    ZN                                                                        *
C    ZN                                                                        *
C                                                                              *
C*****************************************************************************
```

TABLE XII

(continued)

```
1660C
1670      REAL NIT , JGRID
1680C
1690      DIMENSION C(102,6),RT(200),CH(102)
1700C
1710      COMMON /DATA/ NR,      KR(200,7), A(200), S(200),  RTITLE(7),
1720     &              TEMP,   ERR,
1730     &              TSTART,  TSTOP,              PC,       NP,
1740     &              SIG(102),IP(102),    ITYPE(200),       R(200),
1750     &              BK,     SG,                  DILUT
1760      COMMON /NAMES/ SPECIS(102),  REACT(102),  NS
1770      COMMON /FRPLOT/    NIT(3),        SAVCON(100,80),   SAVTIM(80),
1780     &                  NT, JGRID(121,52)
1790      COMMON /STCOM1/N,            T,          H,       HMIN,
1800     &               HMAX,         EPS1,       MF1,     KFLAG1,
1810     &               JSTART
1820      COMMON /STCOM2/YMAX(102)
1830      COMMON /INOUT/ IN,IOUT,ITAPE,I4051,IECHO,ITCS,NTIN,NTWR
1840      COMMON /MODE/ KOUT, LOUT, NTYPE, NPNT, NTAB
1850      COMMON /ASPEN/ NO, ASPEC(102)
1860      COMMON /CONST/ ISPAN, CHOLD(102), CHAR, NK(102), CC(102)
1870      COMMON /IPPM/ PPM, STM, CONV, BLNK, BLNKS
1880      COMMON /ARXN/ ARS(200,7)
1890      COMMON /CHANGE/ NFLG,IND,NCHNG,CHANGE(10),TCHNG(10),KCHNG(10),
1900     &                ACHNG(10,15),SCHNG(10,15),NKC(10,15)
1910      COMMON /STOR/ PA(102)
1920      COMMON /RLIST/ NLR(15), LIST(15,200), NUM, STITLE(15,15)
1930C
1940        DATA TIME/4HTIME/
1950C
1960    2 FORMAT(/,20X,26HSPOT CHECK AT TOTAL TIME =,1PE9.2)
1970    3 FORMAT(/,1X,11H  NET RATES,1X,1P10E12.3 ,/,(13X,1P10E12.3))
1980    4 FORMAT(//,3X,22HTHE REACTION RATES ARE,/,(13X,1P10E12.3))
1990    5 FORMAT(/.5X.5HTIME .4X.10(4X.A4.4X)./.3X.8HINTERVAL,3X,
2000     &       10(4X,A4,4X),/,(14X,10(4X,A4,4X)))
2010   14 FORMAT(1H1)
2020   16 FORMAT(/,5X,5HTIME ,4X,10(4X,A4,4X),/)
2030   21 FORMAT (1X,F12.6,1P10E12.3,/,1X,1P11E12.3,/,(13X,1P10E12.3))
2040   99 FORMAT (1X)
2050  103 FORMAT (/,1X,10H NET RATES,2X,1P5E12.3,/,(13X,1P5E12.3))
2060  104 FORMAT (//,3X,22HTHE REACTION RATES ARE,/,(13X,1P5E12.3))
2070  105 FORMAT (/,5X,5HTIME ,4X,5(4X,A4,4X),/,3X,8HINTERVAL,3X,
2080     & 5(4X,A4,4X),/,(14X,5(4X,A4,4X)))
2090 1011 FORMAT ('0THE LAST PRINT WAS AT:',2X,F15.6,2X,'SECONDS')
2100 1012 FORMAT ('0THE LAST PRINT WAS AT:',2X,F15.6,2X,'MINUTES')
2110 1016 FORMAT (/,5X,5HTIME ,4X,5(4X,A4,4X),/)
2120 1021 FORMAT (1X,F12.6,1P5E12.3,/,1X,1P6E12.3,/,(13X,1P5E12.3))
2130 1071 FORMAT (1X,7A4,1P2E12.3)
2140 1072 FORMAT (6(3X,A4,'.',4X))
2150 1073 FORMAT (1X,F12.6,1P5E12.3,/,(1X,1P6E12.3))
2160 1074 FORMAT (1X,I4)
2170 1075 FORMAT (1X,1P6E12.3)
2180 1080 FORMAT (1X,1PE12.3)
2190 1441 FORMAT('0 ',I2,5X,3(2X,A4),'===>',4(2X,A4),1X,1PE8.2,2X,0PF7.0)
2200 1442 FORMAT('0 0',I1,5X,3(2X,A4),'===>',4(2X,A4),1X,1PE8.2,2X,0PF7.0)
2210C
2220C     ENTER HERE FOR INITIAL CALL
2230C
2240      GO TO (50,55),INDEX
2250   50 INDEX=2
2260      PA(102)=1.
2270      DO 1051 I=1,NS
2280         CH(I)=C(I,1)
2290 1051 CONTINUE
2300C
2310C     TIME INTERVALS
2320C
```

TABLE XII

(continued)

```
2330C
2340        DO 60 I=1,80
2350           SAVTIM(I)=TSTOP*FLOAT(I)/80.
2360 60     CONTINUE
2370C
2380C       INITIALIZE PARAMETERS
2390C
2400        NT=1
2410        NC=0
2420        ZM=C(NS,1)*1.E-20
2430        ZN=ZM*ERR
2440        TSTEP=PC
2450        TPRINT=TLAST
2460        TOLD=T
2470        MS=NQ
2480        NHS=MS
2490        ZM=ZM*1.E-14
2500        TMULT=YMAX(2)
2510        IF(TMULT.GT.1.) TSTEP=0.
2520        MT=19-((NS-1)/10)*3-(NR-1)/30
2530        IF(KOUT.EQ.2) GO TO 1001
2540        IF(NFLG.EQ.0) WRITE (IOUT,14)
2550        NN=NS+1-MIN0(NS/10,1)
2650        NTP=0
2660        IF(NPLOT.EQ.0) GO TO 7
2670        IF(T.EQ.TSTART) GO TO 7
2680        GO TO 42
2690C
2700C       REGULAR ENTRY
2710C
2720    55  IF(T.EQ.TOLD) GO TO 17
2730        IF(NPLOT.EQ.0) GO TO 42
2740        IF(T.LT.SAVTIM(NT)) GO TO 42
2750        SAVTIM(NT)=T
2760        IF(T.GE.TSTOP) SAVTIM(NT)=TSTOP
2770        IF(T.GE.TSTOP) GO TO 10
2780C
2790C       STORE DATA FOR PLOT ROUTINE
2800C
2810        DO 70 I=1,NS
2820           SAVCON(I,NT)=C(I,1)
2830 70     CONTINUE
2840        NT=NT+1
2850    42  IF(T.GE.TLAST) GO TO 10
2860        TOLD=T
2870        DO 6 I=1,N
2880           I1=I
2890C
2900C       CHECK FOR UNREASONABLY LOW CONCENTRATIONS
2910           IF(C(I,1).GE.ZN) GO TO 6
2920C
2930C       INITIATE CALCULATION
2940           IF(T.LT.TSTART+EPS1) GO TO 25
2950C
2960C       IF NEGATIVE CONCENTRATION OCCURS ELIMINATE SPECIES
2970           IF(C(I,1).LT.0.) CALL CLEAN (N0,C,I1)
2980C
2990C       CONCENTRATION IS INCREASING
3000           IF(C(I,2).GE.0.) GO TO 6
3010C
3020C       CHECK FOR MINIMUM CONCENTRATION
3030           IF(-C(I,2).GT.C(I,1)*ZN.OR.C(I,1).LT.ZM) CALL CLEAN (N0,C,I1)
3040           GO TO 6
3050C
3060C       NEGATIVE CONCENTRATIONS ARE NOT ALLOWED
3070    25     IF(C(I,1).LT.0.) C(I,1)=0.
```

TABLE XII

(continued)

```
3080    6 CONTINUE
3090C
3100      DO 999 I=1,NS
3110         IF (CHOLD(I).NE.CHAR) GO TO 999
3120         C(I,1)=CH(I)
3130  999 CONTINUE
3140      IF(T.GE.TPRINT) GO TO 11
3150      NHS=NHS+1
3160C
3170C     NS REGULATES THE NUMBER OF PRINT ITERATIONS ALLOWED BEFORE SPOT
3180C     CHECKING THE CONCENTRATIONS WITH THE RATE INFORMATION
3190C
3200      IF(NHS.GE.NS.OR.T.GE.TLAST) GO TO 7
3210      RETURN
3220    7 NHS=0
3230      NTP=NTP+1
3240      IF(KOUT.EQ.2) GO TO 2077
3250      IF(ISPAN.NE.0) GO TO 1002
3260      IF(NS.GE.11) WRITE(IOUT,21)T,(C(I,1),I=1,10),H,
3270     &              (C(I,1),I=11,NS)
3280      IF(NS.LE.10) WRITE(IOUT,21)T,(C(I,1),I=1,NS),H
3290      GO TO 1003
3300 1002 IF(NS.GE.6) WRITE(IOUT,1021)T,(C(I,1),I=1,5),H,
3310     &              (C(I,1),I=6,NS)
3320      IF(NS.LE.5) WRITE(IOUT,1021)T,(C(I,1),I=1,NS),H
3330 1003 WRITE (IOUT,99)
3340C
3350C *************************************************************
3360C
3370C   STORE DATA FOR PLOTTING ON THE 4051
3380C
3390 2077 IF(NFLG.NE.0) GO TO 1010
3400      NPNT=1
3410      WRITE (I4051,1071) (RTITLE(M),M=1,7), TEMP, DILUT
3420      WRITE (I4051,1072) TIME, (SPECIS(M),M=1,NS)
3430      WRITE (I4051,1073) T,(C(M,1),M=1,NS)
3432C      WRITE (ITEK,1071) (RTITLE(M),M=1,7),TEMP,DILUT
3434C      WRITE (ITEK,1072) TIME,(SPECIS(M),M=1,NS)
3436C      WRITE (ITEK,1073) T,(C(M,1),M=1,NS)
3440C
3450C * STORE NUMBER OF SPECIES AND INITIAL CONCENTRATIONS
3460C * FOR LATER PLOTTING WITH TCS.
3470      WRITE (ITCS,1074) NS+1
3480      WRITE (ITCS,1075) T,(C(I,1),I=1,NS)
3490C
3500C *************************************************************
3510C
3520C     MT REGULATES THE NUMBER OF PRINT ITERATIONS PER PAGE
3530C
3540      IF(NTYPE.EQ.0)GO TO 1010
3550      IF(NTP.GE.MT) GO TO 8
3560      IF(T.GE.TSTOP) GO TO 8
3570 1010 RETURN
3580    8 NTP=0
3590      WRITE(IOUT,2)T
3600C
3610C     CALCULATE THE NET RATES OF REACTION
3620C
3630      CALL DIFFUN (N,C,RT)
3640      RT(NS)=0.
3650      DO 85 I=1,N
3660         RT(NS)=RT(NS)+RT(I)
3670 85   CONTINUE
3680      IF(KOUT.EQ.2) GO TO 2078
3690      IF(ISPAN.EQ.0) WRITE(IOUT,3) (RT(I),I=1,NS)
3700      IF(ISPAN.NE.0) WRITE (IOUT,103) (RT(I),I=1,NS)
```

TABLE XII

(continued)

```
3710C
3720C     COMPUTE THE ACTUAL RATES OF REACTION
3730C
3740 2078 DO 9 I=1,NR
3750         J=KR(I,1)
3760         K=KR(I,2)
3770         L=KR(I,3)
3780         IF(J.EQ.0) RT(I)=0.
3790         IF(J.EQ.0) GO TO 9
3800         IF(J.EQ.99) J=0
3810         IF(J.EQ.0) TJ=1.
3820         IF(J.NE.0) TJ=C(J,1)
3830         IF(K.EQ.0) TK=1.
3840         IF(K.NE.0) TK=C(K,1)
3850         IF(L.EQ.0) TL=1.
3860         IF(L.NE.0) TL=C(L,1)
3870         RT(I)=TJ*R(I)
3880         RT(I)=RT(I)*TK
3890         RT(I)=RT(I)*TL
3900    9 CONTINUE
3910      IF(KOUT.EQ.2) GO TO 1005
3920      IF(ISPAN.EQ.0) WRITE(IOUT,4) (RT(I),I=1,NR)
3930      IF(ISPAN.NE.0) WRITE (IOUT,104) (RT(I),I=1,NR)
3940      IF(NO.NE.0) CALL ARATE (RT)
3950      IF(T.GE.TLAST) RETURN
3960      WRITE(IOUT,14)
3970      NN=NS+1-MIN0(NS/10,1)
3980      IF(ISPAN.NE.0) GO TO 1004
3990      IF(NN.GE.11) WRITE(IOUT,5)(SPECIS(I),I=1,NN)
4000      IF(NN.LE.10) WRITE(IOUT,16)(SPECIS(I),I=1,NN)
4010      GO TO 1005
4020 1004 NN=NS+1-MIN0(NS/5,1)
4030      IF(NN.GE.6) WRITE(IOUT,105)(SPECIS(I),I=1,NN)
4040      IF(NN.LE.5) WRITE(IOUT,1016)(SPECIS(I),I=1,NN)
4050 1005 RETURN
4060C
4070C     INTERPOLATE TO EXACT TIME DESIRED FOR PRINTING OUTPUT
4080C     AT THE LAST TIME STEP
4090C
4100   10 NHS=NS
4110      NTP=0
4120      IF(NCHNG.NE.0) GO TO 11
4130      TPRINT=TLAST
4140C
4150C     INTERPOLATE FOR THE EXACT TIME DESIRED TO PRINT
4160C
4170   11 IF(TPRINT.LT.TSTART) GO TO 15
4180      RR=(TPRINT-T)/H
4190      DO 12 I=1,N
4200      PA(I)=C(I,1)
4210      RH=1.
4220      DO 12 J=1,NQ
```

TABLE XII

(continued)

```
4230          RH=RH*RR
4240          IF (CHOLD(I).EQ.CHAR) GO TO 12
4250          PA(I)=PA(I)+RH*C(I,J+1)
4260    12 CONTINUE
4270       IF(TPRINT.NE.TLAST) GO TO 95
4280       DO 90 I=1,NS
4290          SAVCON(I,NT)=PA(I)
4300 90    CONTINUE
4310C
4320C      CALCULATE THE NET RATES OF REACTION
4330C
4340    95 CALL DIFFUN (N,PA,RT)
4350       IF(KOUT.EQ.2) GO TO 2079
4360       IF(ISPAN.NE.0) GO TO 1007
4370       IF(NS.LE.10) WRITE(IOUT,21)TPRINT,(PA(I),I=1,NS),H
4380       IF(NS.GE.11) WRITE(IOUT,21)TPRINT,(PA(I),I=1,10),H,
4390      &             (PA(I),I=11,NS)
4400       GO TO 1008
4410 1007 IF(NS.LE.5) WRITE(IOUT,1021)TPRINT,(PA(I),I=1,NS),H
4420       IF(NS.GE.6) WRITE(IOUT,1021)TPRINT,(PA(I),I=1,5),H,
4430      &              (PA(I),I=6,NS)
4440 1008 IF(KOUT.EQ.0) GO TO 1015
4450       IF(PPM.EQ.BLNK) WRITE (NTWR,1011) TPRINT
4460       IF(PPM.NE.BLNK) WRITE (NTWR,1012) TPRINT
4470 1015 RT(NS)=0.
4480       DO 80 I=1,N
4490          RT(NS)=RT(NS)+RT(I)
4500 80    CONTINUE
4510       IF(ISPAN.EQ.0) WRITE(IOUT,3) (RT(I),I=1,NS)
4520       IF(ISPAN.NE.0) WRITE (IOUT,103) (RT(I),I=1,NS)
4530C
4540 2079 NPNT=NPNT+1
4550C
4560C *************************************************************
4570C   STORE DATA FOR PLOTTING ON THE 4051
4580       WRITE (I4051,1073) TPRINT, (PA(M),M=1,NS)
4585C       WRITE (ITEK,1073) TPRINT,(PA(M),M=1,NS)
4590C
4600C STORE DATA FOR PLOTTING ON HONEYWELL (TCS)
4610       WRITE (ITCS,1075) TPRINT, (PA(M),M=1,NS)
4620C *************************************************************
4630C
4640C
4650C      COMPUTE THE ACTUAL RATES OF REACTION
4660C
4670       DO 13 I=1,NR
4680          J=KR(I,1)
4690          K=KR(I,2)
4700          L=KR(I,3)
4710          IF(J.EQ.0) RT(I)=0.
4720          IF(J.EQ.0) GO TO 13
4730          IF(J.EQ.99) J=102
4740          IF(K.EQ.0) K=102
4750          IF(L.EQ.0) L=102
4760          RT(I)=R(I)*PA(J)
```

TABLE XII

(continued)

```
4770         RT(I)=RT(I)*PA(K)
4780         RT(I)=RT(I)*PA(L)
4790    13 CONTINUE
4800       IF(KOUT.EQ.2) GO TO 1330
4810       IF(ISPAN.EQ.0) WRITE(IOUT,4) (RT(I),I=1,NR)
4820       IF(ISPAN.NE.0) WRITE (IOUT,104) (RT(I),I=1,NR)
4830       IF(NO.NE.0) CALL ARATE (RT)
4840       IF(NCHNG.EQ.0.OR.CHANGE(IND+1).EQ.0.) GO TO 1330
4850       IF(T.LT.CHANGE(IND+1)) GO TO 1330
4860       IND=IND+1
4870       TSTEP=TCHNG(IND)
4880       YMAX(1)=TSTEP
4890       PC=TSTEP
4900       IF(KOUT.EQ.2) GO TO 1079
4910       WRITE (IOUT,14)
4920  1079 IF(KCHNG(IND).EQ.0) GO TO 1330
4930       DO 1321 K1=1,KCHNG(IND)
4940          A(NKC(IND,K1))=ACHNG(IND,K1)
4950          S(NKC(IND,K1))=SCHNG(IND,K1)
4960          NSLOT=NKC(IND,K1)
4970          IF(NSLOT.LE.9) WRITE (IOUT,1442) NSLOT,
4980      &     (ARS(NSLOT,MO),MO=1,7), A(NSLOT), S(NSLOT)
4990          IF(NSLOT.GT.9.AND.NSLOT.LE.99) WRITE (IOUT,1441)
5000      &     NSLOT, (ARS(NSLOT,MO),MO=1,7),
5010      &     A(NSLOT), S(NSLOT)
5020          WRITE (IOUT,99)
5030  1321 CONTINUE
5040       NFLG=9
5050       GO TO 15
5060  1330 NHS=0
5070       IF(T.GE.TLAST) RETURN
5080       IF(KOUT.EQ.2) GO TO 15
5090       IF(KOUT.NE.1) GO TO 1318
5100       IF(NTYPE.EQ.0) GO TO 1340
5110       NTP=NTP+6
5120       IF(NTP.GT.MT) WRITE(IOUT,14)
5130       IF(NTP.GT.MT) NTP=0
5140       GO TO 1318
5150  1340 NPAGE=((5*NO)+(NR/10)+(3*(NS/10))+(4*NUM)+12)
5160       IF(NPAGE.GT.30) WRITE(IOUT,14)
5170  1318 NN=NS+1-MIN0(NS/10,1)
5180       IF(ISPAN.NE.0) GO TO 1009
5190       IF(NN.GE.11) WRITE(IOUT,5)(SPECIS(I),I=1,NN)
5200       IF(NN.LE.10) WRITE(IOUT,16)(SPECIS(I),I=1,NN)
5210       GO TO 15
5220  1009 NN=NS+1-MIN0(NS/5,1)
5230       IF(NN.GE.6) WRITE(IOUT,105)(SPECIS(I),I=1,NN)
5240       IF(NN.LE.5) WRITE(IOUT,1016)(SPECIS(I),I=1,NN)
5250    15 TPRINT=TPRINT*TMULT + TSTEP
5260    17 RETURN
5270       END
```

TABLE XIII

CHEMK "MAIN" SUBROUTINE

```
1300C      SUBROUTINE MAIN
1301C
1302C
1303c
1310       REAL IBLANK ,MBLANK ,JINTER
1320       REAL JBLANK ,JSTAR ,JPLUS ,JBAR ,NPLOT
1330       REAL IRS ,ITITLE,NIT ,JVERT ,JGRID
1340       REAL NARR
1350C
1360C IGO(4) CHANGED TO RIGO(4) FOR IMPLICIT TYPING
1370C
1380C RIGO(4) CONTAINS THE SELECTIONS TO BE MADE AT
1390C         AT THE END OF THE RUN, VIZ. MORE, CONT
1400C         MODK, OR HALT.
1410C
1420       DIMENSION YSTOR(3)
1430C
1440       COMMON /DATA/ NR,     KR(200,7), A(200), S(200),  ITITLE(7),
1450      &              TEMP,   ERR,
1460      &              TSTART,  TSTOP,            PC,      NP,
1470      &              SIG(102),IP(102),    ITYPE(200),     R(200),
1480      &              BK,     SG,                        DILUT
1490       COMMON /NAMES/     SPECIS(102),    REACT(102),      NS
1500       COMMON /FRPLOT/    NIT(3),        SAVCON(100,80),   SAVTIM(80),
1510      &                  NT, JGRID(121,52)
1520       COMMON /ALPHA/     RIGO(4),        IBLANK,          MBLANK,
1530      &                   JINTER
1540       COMMON /APLOT/     JVERT(52,2),   JBLANK,           JSTAR,
1550      &                   JPLUS,         JBAR
1560       COMMON /STCOM1/    N,             T,               GUESS,
1570      &                   HMIN,          HMAX,            EPS1,
1580      &                   MF1,           KFLAG1,          JSTART
1590       COMMON /STCOM2/    YMAX(102)
1600       COMMON /STCOM3/    ERROR(102)
1610       COMMON /STCOM4/ PW(10404),     IW(102)
1620       COMMON /STCOM5/    FSAVE(204)
1630       COMMON /INOUT/ IN,IOUT,ITAPE,I4051,IECHO,ITCS,NTIN,NTWR
1640       COMMON /MODE/ KOUT, LOUT, NTYPE, NPNT, MTAB
1650       COMMON /CODES/ ICODE(200)
1660       COMMON /ASPEN/ NO, ASPEC(102)
1670       COMMON /IPPM/ PPM, STM, CONV, BLNK, BLNKS
1680       COMMON /ARXN/ ARS(200,7)
1690       COMMON /RXNS/ RXN(9,601)
1700       COMMON /RLIST/ NLR(15), LIST(15,200), NUM, STITLE(15,15)
1710       COMMON /CONST/ ISPAN, CHOLD(102), CHAR, NK(102), CC(102)
1720       COMMON /HOLD/ IRS(200,7), C(612), ATAB(102), REAM(102), COLD(102)
1730       COMMON/CHANGE/NFLG,IND,NCHNG,CHANGE(10),TCHNG(10),KCHNG(10),
1740      & ACHNG(10,15),SCHNG(10,15),NKC(10,15)
1750       COMMON /STOR/ PA(102)
1760       COMMON /TITLE/ RGO(16), INDX
1770       COMMON /DEBUG/ JDBTYP,JDBLUN,JDBMSC
1780C
1790C
1800C   REACTION LIBRARY
```

TABLE XIII

(continued)

```
1810C
1820C
1830C     ALPHAMERIC DATA
1840      DATA RIGO(1)/4HMORE/, RIGO(2)/4HCONT/, RIGO(3)/4HMODK/,
1850     &     RIGO(4)/4HHALT /, IBLANK/4H    /, MBLANK/4HM   /,
1860     &     JINTER/4HINTV/
1870      DATA RGO/'LIBR','NOXX','NOXW','PROH','PROP','CLOX','METH',
1880     & 'HONO','BUTA','BUPR','MANU','TOLH','MODK','FIL1','FIL2','FIL3'/
1890      DATA JVERT/18*4H    ,4H C  ,          4H O  ,       4H N  ,
1900     &              4H C  ,4H E  ,          4H N  ,       4H T  ,
1910     &              4H R  ,4H A  ,          4H T  ,       4H I  ,
1920     &              4H O  ,4H N  ,          4H    ,       4H P  ,
1930     &              4H P  ,4H M  ,          69*4H   /
1940      DATA JBLANK/4H    /, JSTAR/1H*/,     JPLUS/1H+/,   JBAR/1HI/
1950      DATA HALT/4HHALT/, STOP/4HSTOP/, OFF/4H$OFF/
1960      DATA ALL/4HALL /
1970      DATA EQUAL/1H=/, CHAR/1HH/
1980      DATA STN/60./, CONV/2.45E+13/, BLNK/1H /, BLNKS/4H    /
1990      DATA BELLS/4H    /
2000      DATA TOP/1.00E+38/
2010C
2020C NTWR  -  TERMINAL OUTPUT LUN
2030C NTIN  -  TERMINAL INPUT LUN
2040C NPWR  -  PRINTER OUTPUT LUN (DEFAULT = NTWR)
2050C IECHO -  LUN FOR ECHOING "TERMINAL" RESPONSES IN BATCH MODE
2060C          DEFAULT = NTWR
2070C I4051 -  LUN FOR TEK 4051 FORMAT OUTPUT FILE
2080C ITCS  -  OUTPUT LUN FOR TCS PLOTTING DATA
2090C IOUT  -  LUN FOR PRINTING CALCULATED OUTPUT (DEFAULT = NTWR)
2100C JOUT  -  LUN FOR PRINTING REACTION MECHANISMS (DEFAULT = NTWR)
2110C
2120      NTIN=07
2130      NTWR=06
2140      I4051=30
2150      ITCS=31
2155C      ITEK=33
2160C
2170      IOUT=NTWR
2180      JOUT=NTWR
2190      NPWR=NTWR
2200      IECHO=NTWR
2210C
2220C     INITIAL PARAMETERS
2230C
2240C
2250C     CLEAR PATTERN MATRIX AND SET THE FIRST ELEMENTS
2260C
2270  890 DO 20 J=1,200
2280      DO 20 K=1,7
2290   20 KR(J,K)=0
2300      DO 25 J=1,200
2310      A(J)=0.
```

TABLE XIII

(continued)

```
      R(J)=0.
   25 S(J)=0.
      NCHNG=0
      IND=0
      DO 26 M=1,10
      KCHNG(M)=0
   26 CONTINUE
      MTAB=0
      NEW=0
      N=0
      NR=0
      NS=1
   80 NS=NS-1
C
C     NX = LAST NUMBER OF THE REACTION SEQUENCE
C     NPLOT = PLOT OPTION
C     DILUT= DILUTION FACTOR
C
C*****************************************************************
C**********    T E R M I N A L     M O D E     I N P U T     ***
C
C    NADRXN ..... THE NUMBER OF ADDITIONAL REACTION SEQUENCES
C    NX ....... THE TOTAL NUMBER OF REACTIONS
C    ICODE .... CONTAINS THE CODE NUMBERS FOR ALL REACTIONS
C               THAT COME FROM THE LIBRARY
C
 1030 CONTINUE
      YMAX(3)=0.
      JPLOT=0
C
C  FORMFEED TO SEPARATE OUTPUT FROM BATCH DATA
      WRITE (NTWR,2730)
 2730 FORMAT (1H1)
C
C   DETERMINE FIELD SIZE
C
      WRITE (NTWR,2000)
 2000 FORMAT (1X,'ENTER A NON-ZERO NUMBER (I1) IF THE FIELD ',
     &           ' SIZE IS LESS THAN 132:')
      READ (NTIN,2010) ISPAN
 2010 FORMAT (1X,I1)
      WRITE (IECHO,2010) ISPAN
C
C   ARE THE UNITS TO BE ABSOLUTE OR PPM?
C
      WRITE (NTWR,2020)
 2020 FORMAT (1X,'ENTER AN ALPHANUMERIC (A1) IF PPM UNITS'/
     &           'ARE TO BE USED. THEN, IF THE PRESSURE IS'/
     &           'NOT 760 TORR, ENTER THE TOTAL PRESSURE'/
     &           'IN TORR (F7.2):')
      READ (NTIN,2030) PPM,PRESS
```

TABLE XIII

(continued)

```
2830 2030 FORMAT (1X,A1,F7.2)
2840 3345 WRITE (IECHO,2030) PPM,PRESS
2850C
2860      IF (PRESS.NE.0.) CONV=CONV*(PRESS/760.)
2870C
2880C   CHOOSE REACTION SCHEME(S)
2890C
2900      NX=0
2910      NNY=1
2920      INDX=0
2930 1012 WRITE (NTWR,2040)
2940 2040 FORMAT (1X,'ENTER THE NAME OF THE DESIRED REACTION'/
2950     &        1X,'SCHEME (A4). IF ENTERING MULTIPLE SCHEMES'/
2960     &        1X,'SEPARATE BY A SPACE.'/
2970     &        1X,'LIBR, NOXX, NOXW, PROH, PROP, CLOX,'/
2980     &        1X,'METH, HONO, BUTA, BUPR, MANU, TOLH,'/
2990     &        1X,'FIL1, FIL2, FIL3.')
3000      READ (NTIN,2050) (ITITLE(I),I=1,7)
3010 2050 FORMAT (1X,7(A4,1X))
3020      WRITE (IECHO,2050) (ITITLE(I),I=1,7)
3030C
3040 1013 INDX=INDX+1
3050C  RGO(1) = LIBR
3060      IF(ITITLE(INDX).EQ.RGO(1)) CALL LIBR
3070C  RGO(2) = NOXX
3080      IF(ITITLE(INDX).EQ.RGO(2)) CALL NOXX (NX,IRS)
3090C  RGO(3) = NOXW
3100      IF(ITITLE(INDX).EQ.RGO(3)) CALL FILE (NX,IRS)
3110C  RGO(4) = PROH
3120      IF(ITITLE(INDX).EQ.RGO(4)) CALL PROH (NX,IRS)
3130C  RGO(5) = PROP
3140      IF(ITITLE(INDX).EQ.RGO(5)) CALL FILE (NX,IRS)
3150C  RGO(6) = CLOX
3160      IF(ITITLE(INDX).EQ.RGO(6)) CALL CLOX (NX,IRS)
3170C  RGO(7) = METH
3180      IF(ITITLE(INDX).EQ.RGO(7)) CALL METH (NX,IRS)
3190C  RGO(8) = HONO
3200      IF(ITITLE(INDX).EQ.RGO(8)) CALL HONO (NX,IRS)
3210C  RGO(9) = BUTA
3220      IF(ITITLE(INDX).EQ.RGO(9)) CALL FILE (NX,IRS)
3230C  RGO(10)= BUPR
3240      IF(ITITLE(INDX).EQ.RGO(10)) CALL FILE (NX,IRS)
3250C  RGO(11)= MANU
3260      IF(ITITLE(INDX).EQ.RGO(11)) CALL MANUAL (NX,IRS)
3270C  RGO(12)= TOLH
3280      IF(ITITLE(INDX).EQ.RGO(12)) CALL FILE (NX,IRS)
3290C  RGO(13)= MODK
3300      IF(ITITLE(INDX).EQ.RGO(13)) YMAX(3)=1.
3310      IF(ITITLE(INDX).EQ.RGO(13)) JPLOT=1
3320C  RGO(14)= FIL1
3330      IF(ITITLE(INDX).EQ.RGO(14)) CALL FILE (NX,IRS)
3340C  RGO(15)= FIL2
```

TABLE XIII

(continued)

```
      IF(ITITLE(INDX).EQ.RGO(15)) CALL FILE (NX,IRS)
C  RGO(16)= FIL3
      IF(ITITLE(INDX).EQ.RGO(16)) CALL FILE (NX,IRS)
C
      IF(ITITLE(INDX+1).NE.BLNKS) GO TO 1013
C
C     ADDITIONAL RXN SEQUENCES
C
 1680 WRITE (NTWR,2060)
 2060 FORMAT (1H0,'ENTER THE NUMBER OF (ADDITIONAL) REACTION ',
     &            'SEQUENCES (I3):')
      READ (NTIN,2070) NADRXN
 2070 FORMAT (1X,I3)
      WRITE (IECHO,2070) NADRXN
C
      IF(NADRXN.GE.99) GO TO 1012
      IF(NADRXN.EQ.0) GO TO 1460
C
C   REACTION INPUT DATA
C
      WRITE (NTWR,2080)
 2080 FORMAT (1H0,'ENTER CODE NUMBERS FOR THE ADDITIONAL REACTION '/
     &            'SEQUENCES (I3) SEPARATED BY A (CR):')
      READ (NTIN,2090) (ICODE(I), I=1,NADRXN)
 2090 FORMAT (1X,I3)
      WRITE (IECHO,2090) (ICODE(I), I=1,NADRXN)
C
      CALL SETUP (NADRXN,NX,IRS)
C
C
C   ESTABLISH REACTION MATRIX
C
 1460 CALL MATRX (C,IRS)
C
C   SPECIFY START TIME, PRINTING PARAMETERS, END TIME
C
      WRITE (NTWR,2150)
 2150 FORMAT (1H0,'ENTER THE STARTING TIME (F12.5), ',
     &            'DEFAULT IS ZERO (0.):')
      READ (NTIN,2160) TSTART
 2160 FORMAT (1X,F12.5)
      WRITE (IECHO,2160) TSTART
C
      WRITE (NTWR,2100)
 2100 FORMAT (1H0,'ENTER THE INITIAL TIME OF PRINT (F12.5):')
      READ (NTIN,2105) TPRINT
 2105 FORMAT (1X,F12.5)
      WRITE (IECHO,2105) TPRINT
C
```

TABLE XIII

(continued)

```
      WRITE (NTWR,2110)
2110 FORMAT (1H0,'ENTER THE TIME INTERVAL (F12.5), ',
     &            'DEFAULT IS THE INITIAL TIME OF PRINT:')
      READ (NTIN,2120) TSTEP
2120 FORMAT (1X,F12.5)
      WRITE (IECHO,2120) TSTEP
C
      WRITE (NTWR,2130)
2130 FORMAT (1H0,'ENTER THE TIME MULTIPLE BETWEEN SUBSEQUENT'/
     &           'PRINTS (F12.5), DEFAULT IS ONE (1.):')
      READ (NTIN,2140) TMULT
2140 FORMAT (1X,F12.5)
      WRITE (IECHO,2140) TMULT
C
      WRITE (NTWR,2170)
2170 FORMAT (1H0,'ENTER THE ENDING TIME (F12.5):')
      READ (NTIN,2180) TSTOP
2180 FORMAT (1X,F12.5)
      WRITE (IECHO,2180) TSTOP
C
      TPN=TPRINT
      IF (TSTEP .EQ. 0.) TSTEP=TPRINT
      IF (TPRINT.EQ.0.) TPRINT=1.E37
      IF (TSTOP.EQ.0.) TSTOP=10.*TPRINT
      NPRNT=10000
      ERR=1.00E-02
      IF(TSTOP.EQ.0.) TSTOP=10.*TPRINT
C
C "CONTINUE" RE-ENTRY
1600 CONTINUE
C
C  ENTER TEMPERATURE AND DILUTION FACTOR
C
      WRITE (NTWR,2190)
2190 FORMAT (1H0,'ENTER THE TEMPERATURE (F12.5), DEFAULT = 300.:')
      READ (NTIN,2200) TEMP
2200 FORMAT (1X,F12.5)
      WRITE (IECHO,2200) TEMP
C
      IF(TEMP.EQ.0.) TEMP=300.
C
      WRITE (NTWR,2210)
2210 FORMAT (1H0,'ENTER THE DILUTION FACTOR (E8.2):')
      READ (NTIN,2220) DILUT
2220 FORMAT (1X,E8.2)
      WRITE (IECHO,2220) DILUT
C
C     SET LIMITS FOR TIMED OUTPUTS
C
      IF(TSTEP.NE.0.) YMAX(1)=TSTEP
      IF(TSTEP.NE.0.) PC=TSTEP
      IF(TSTEP.EQ.0.) PC=1.E38
      IF(TSTEP.EQ.0.) YMAX(1)=1.E38
```

TABLE XIII

(continued)

```
      IF(TMULT.NE.0.) YMAX(2)=TMULT
      IF(TMULT.EQ.0.) YMAX(2)=1.
C
C     OUTPUT DEVICE SELECTION
C     KOUT  FOR CALCULATED OUTPUT PRINTING
C     LOUT  FOR REACTION SCHEME PRINTING
C     0   AT TERMINAL
C     1   AT LINE PRINTER
C     2   NOT PRINTED
C
      WRITE (NTWR,2230)
 2230 FORMAT (1H0,'IF YOU WANT THE REACTION SCHEME AND/OR ',
     &            'THE OUTPUT TO BE SENT TO THE LINEPRINTER,'/
     &          1X,'ENTER:   00 (OR A CR) FOR NEITHER, OR'/
     &          1X,'         01  FOR THE REACTION SCHEME ONLY, OR'/
     &          1X,'         02  FOR NO PRINTING OF THE REACTION ',
     &                                                 'SCHEME, OR'/
     &          1X,'         10  FOR THE OUTPUT ONLY, OR'/
     &          1X,'         11  FOR BOTH SENT TO THE LINEPRINTER.')
      READ (NTIN,2240) KOUT,LOUT
 2240 FORMAT (1X,2I1)
      WRITE (IECHO,2240) KOUT,LOUT
C
C  IOUT AND JOUT DEFAULT TO NTWR
      IF(KOUT.EQ.1) IOUT=NPWR
      IF(LOUT.EQ.1) JOUT=NPWR
      IF(KOUT.NE.0.AND.ISPAN.NE.0) ISPAN=0
C
C   PRINT THE REACTION SCHEMES USED
C
      IF(LOUT.EQ.2) GO TO 1445
C  IF NOT "MORE" AND NOT "CONTINUE", THEN FIRST TIME THROUGH
      IF (ITITLE(1) .NE. RIGO(1) .AND. ITITLE(1) .NE. RIGO(2)) GO TO 1009
C IF "CONTINUE", DON'T PRINT REACTIONS
      IF(ITITLE(1) .EQ. RIGO(2)) GO TO 1445
      IF (ITITLE(1) .EQ. RIGO(1) .AND. NADRXN .EQ. 0) GO TO 1445
      GO TO 1447
C
C  PRINT REACTION SCHEME TITLE(S) & REACTIONS
 1009 WRITE (JOUT,2250) (ITITLE(I),I=1,7)
 2250 FORMAT (1H0,'THE REACTIONS IN THE ',7(A4,1X)/1X,'SCHEME(S) ARE:')
 1447 DO 1440 I=NNY,NX
      WRITE (JOUT,2280) I, (ARS(I,M),M=1,3),
     & (ARS(I,M),M=4,7), A(I), S(I)
 2280 FORMAT (1X,I3,5X,3(2X,A4),'===>',4(2X,A4),1X,1PE8.2,2X,0PF7.0)
 1440 CONTINUE
C
C   MAKE ANY CHANGES IN K
C
 1445 WRITE (NTWR,2290)
 2290 FORMAT (//1X,'IF ANY RATE CONSTANTS ARE TO BE CHANGED, ENTER THE'/
```

TABLE XIII

(continued)

```
4380      &           1X,'REACTION NUMBER (I2), AN EQUALS SIGN, AND THE NEW'/
4890      &           1X,'RATE CONSTANT FOR EACH CHANGE BY ENTERING THE PRE-'/
4900      &           1X,'EXPONENTIAL FACTOR (E8.2), A COMMA, AND THEN THE'/
4910      &           1X,'ACTIVATION ENERGY (F10.0).'/
4920      &           1X,'E.G.: 13=4.85E-13,-510.',5X,
4930      &             'INDICATE COMPLETION BY ENTERING A CR ONLY.'/)
4940 1450 READ (NTIN,2300) NK(NEW+1), NARR, ACT
4950 2300 FORMAT (1X,I2,1X,E8.2,1X,F10.0)
4960      WRITE (IECHO,2300) NK(NEW+1), NARR, ACT
4970C
4980      IF(NK(NEW+1).EQ.0) GO TO 1475
4990      NEW=NEW+1
5000      A(NK(NEW))=NARR
5010      S(NK(NEW))=ACT
5020      GO TO 1450
5030C
5040 1475 IF(NEW.EQ.0) GO TO 1310
5050C  WRITE OUT REACTIONS WITH CHANGED RATE CONSTANTS
5060      DO 1455 I=1,NEW
5070      WRITE (IOUT,2280) NK(I), (ARS(NK(I),M),M=1,3),
5080     & (ARS(NK(I),M),M=4,7), A(NK(I)), S(NK(I))
5090C
5100 1455 CONTINUE
5110C
5120      IF(LOUT.NE.1) GO TO 1310
5130C IF ONLY ONE PRINTING OUTPUT, SKIP THIS PRINTING
5140      IF (JOUT .EQ. NTWR) GO TO 1310
5150      WRITE (JOUT,2580)
5160 2580 FORMAT (1X,////)
5170      DO 1456 I=1,NEW
5180      WRITE (JOUT,2280) NK(I), (ARS(NK(I),M),M=1,3),
5190     & (ARS(NK(I),M),M=4,7), A(NK(I)), S(NK(I))
5200 1456 CONTINUE
5210C
5220C   ENTER ANY RATE CONSTANT CHANGES TO BE MADE DURING THE PROGRAM
5230C
5240 1310 WRITE (NTWR,2310)
5250 2310 FORMAT (1H0,'IF YOU WISH TO CHANGE ANY RATE CONSTANTS, (E.G. LIGHTS'/
5260     &            'ON/OFF), AND/OR THE TIME INTERVAL DURING THE PROGRAM'/
5270     &            'RUN, ENTER THE NUMBER OF TIMES THAT THERE WILL BE'/
5280     &            'A CHANGE (I1); DEFAULT IS NO CHANGES:')
5290      READ (NTIN,2320) NCHNG
5300 2320 FORMAT (1X,I1)
5310      WRITE (IECHO,2320) NCHNG
5320C
5330      IF(NCHNG.EQ.0) GO TO 1470
5340C
5350      WRITE (NTWR,2330)
5360 2330 FORMAT (1X,'ENTER THE TIMES DURING THE PROGRAM RUN AT WHICH'/
5370     &        1X,'THERE WILL BE A CHANGE IN THE RATE AND/OR INTERVAL.'/
5380     &        1X,'INCLUDE THE DECIMAL POINT (F10.4) E.G. 10256.3451   .')
5390      READ (NTIN,2340) (CHANGE(K),K=1,NCHNG)
5400 2340 FORMAT (1X,F10.4)
5410      WRITE (IECHO,2340) (CHANGE(K),K=1,NCHNG)
5420C
```

TABLE XIII

(continued)

```
5430       WRITE (NTWR,2350)
5440 2350 FORMAT (1X,'ENTER THE TIME INTERVALS TO BE USED DURING THE PROGRAM'/
5450     &         1X,'RUN FOLLOWING THE TIMES LISTED ABOVE.'/
5460     &         1X,'INCLUDE THE DECIMAL POINT (F10.4):')
5470       READ (NTIN,2360) (TCHNG(K),K=1,NCHNG)
5480 2360 FORMAT (1X,F10.4)
5490       WRITE (IECHO,2360) (TCHNG(K),K=1,NCHNG)
5500C
5510       DO 1317 M=1,NCHNG
5520       IF(TCHNG(M).EQ.0.0) TCHNG(M)=TSTEP
5530 1317 CONTINUE
5540C
5550       WRITE (NTWR,2370)
5560 2370 FORMAT (1X,'ENTER THE NUMBER OF THE REACTION AND THE RATE '/
5570     &         1X,'CONSTANT FOR EACH CHANGE. FOLLOW THE PROCEDURE AS '/
5580     &         1X,'ABOVE FOR RATE CONSTANT CHANGES.'/
5590     &         1X,'(E.G.: 03=4.85E-13,-510.)',5X,
5600     &            'INDICATE COMPLETION BY ENTERING A CR ONLY.'/)
5610       DO 1315 M=1,NCHNG
5620       WRITE (NTWR,2380) CHANGE(M)
5630 2380 FORMAT (1X,'ENTER THE RATE CONSTANTS FOR TIME: ',F15.7,/)
5640 1316 READ (NTIN,2620) NKC(M,(KCHNG(M)+1)),ACHNG(M,(KCHNG(M)+1)),
5650     &       SCHNG(M,(KCHNG(M)+1))
5660 2620 FORMAT (1X,I2,1X,E8.2,1X,F10.0)
5670       WRITE (IECHO,2620) NKC(M,(KCHNG(M)+1)), ACHNG(M,(KCHNG(M)+1)),
5680     &         SCHNG(M,(KCHNG(M)+1))
5690       IF(NKC(M,(KCHNG(M)+1)).EQ.0) GO TO 1315
5700       KCHNG(M)=KCHNG(M)+1
5710       GO TO 1316
5720 1315 CONTINUE
5730C      .
5740C   CONC OF SPECIES INITIALLY PRESENT
5750C
5760 1470 NTAB=NTAB+1
5770       IF(NTAB.GT.1) GO TO 1503
5780       WRITE (NTWR,2390)
5790 2390 FORMAT (1H0,'ENTER ANY REACTANT WITH AN INITIAL NON-ZERO '/
5800     &         1X,'CONCENTRATION (A4), AN EQUALS SIGN,'/
5810     &         1X,'AND THEN ITS INITIAL CONCENTRATION (E8.2):'/
5820     &         1X,'(E.G. O2  =5.19E+18)',8X,
5830     &            'INDICATE COMPLETION BY ENTERING A CR ONLY.'/)
5840 1500 READ (NTIN,2400) REACT(N+1), COLD(N+1), C(N+1)
5850 2400 FORMAT (1X,A4,A1,E8.2)
5860       WRITE (IECHO,2400) REACT(N+1), COLD(N+1), C(N+1)
5870C
5880       IF (REACT(N+1).EQ.IBLANK) GO TO 1502
5890       N=N+1
5900       GO TO 1500
5910C
5920C       RE-INITIALIZE THE CONCENTRATIONS ON A MORE OR CONT OPTION
5930C
5940 1503 IF(ITITLE(1).NE.RIGO(2)) WRITE (NTWR,2410)
5950 2410 FORMAT (/,1X/'THE SPECIES WITH INITIAL NON-ZERO CONCENTRATIONS ',
```

TABLE XIII

(continued)

```
5960      &         'FROM THE LAST RUN ARE:',//)
5970       IF (ITITLE(1).EQ.RIGO(2)) WRITE (NTWR,2420)
5980 2420 FORMAT (/,1X/'THE NEW INITIAL CONCENTRATIONS (FROM THE LAST ',
5990      &         'RUN) WILL BE:')
6000 1505 DO 1485 I=1,N
6010       ATAB(I)=EQUAL
6020       IF (COLD(I).EQ.CHAR) ATAB(I)=CHAR
6030C  PRINT OUT CURRENT STARTING REACTANT CONCENTRATIONS
6040       WRITE (NTWR,2440) I,REACT(I),ATAB(I),C(I)
6050 2440 FORMAT (1X,I2,1X,A4,A1,1PE8.2)
6060 1485 CONTINUE
6070C
6080       WRITE (NTWR,2450)
6090 2450 FORMAT (//'ENTER ANY CHANGES IN THE LIST BY ENTERING THE'/
6100      &          ' NUMBER (I2), A SPACE, THE SPECIES (A4), AN EQUALS'/
6110      &          ' SIGN, AND THEN THE NEW CONCENTRATION (E8.2):'/
6120      &          ' (E.G.: 04 O2  =5.19E+18)'/
6130      &          ' *'/
6140      &          ' ENTER ANY ADDITIONS TO THE LIST BY ENTERING A'/
6150      &          ' ZERO-ZERO (00) INSTEAD OF A NUMBER FROM THE LIST.'/
6160      &          ' (E.G.: 00 CL2 =2.00E+11)',6X,
6170      &          ' INDICATE COMPLETION BY ENTERING A CR ONLY.'/)
6180 1484 READ (NTIN,2460) NC, DREACT, RCOLD, CCC
6190 2460 FORMAT (1X,I2,1X,A4,A1,E8.2)
6200       WRITE (IECHO,2460) NC, DREACT, RCOLD, CCC
6210C
6220       IF (DREACT.EQ.IBLANK) GO TO 1502
6230       IF(NC.NE.0) GO TO 1487
6240       N=N+1
6250       NC=N
6260 1487 REACT(NC)=DREACT
6270       C(NC)=CCC
6280       COLD(NC)=RCOLD
6290       GO TO 1484
6300C
6310C  IS THIS A CONT(INUED) REACTION ?
6320 1502 IF(ITITLE(1).EQ.RIGO(2)) GO TO 1489
6330       NI=N
6340       NM=N
6350 1489 DO 9488 I=1,N
6360       CC(I)=C(I)
6370       REAM(I)=REACT(I)
6380       IF (COLD(I).NE.CHAR) GO TO 9488
6390       DO 1488 J=1,NS
6400       CHOLD(J)=0.
6410       IF (SPECIS(J).EQ.REACT(I)) CHOLD(J)=CHAR
6420 1488 CONTINUE
6430 9488 CONTINUE
6440C
6450       WRITE (NTWR,2470)
6460 2470 FORMAT (' IF YOU WANT THE ACTUAL RATES ALSO PRINTED FOR A'/
6470      &          ' SELECTED SPECIES, ENTER EACH SPECIES '/
6480      &          ' FOLLOWED BY A CR. ENTER "ALL" IF THE RATES '/
6490      &          ' FOR ALL SPECIES ARE TO BE LISTED.'/
```

TABLE XIII

(continued)

```
6500      &        ' INDICATE COMPLETION BY ENTERING A CR ONLY.'/)
6510       NO=-1
6520   185 NO=NO+1
6530   180 READ (NTIN,2480) ASPEC(NO+1)
6540  2480 FORMAT (1X,A4)
6550       WRITE (IECHO,2480) ASPEC(NO+1)
6560C
6570       IF (ASPEC(NO+1).EQ.IBLANK) GO TO 187
6580       IF (ASPEC(NO+1).NE.ALL) GO TO 185
6590       NO=NS-1
6600       DO 182 I=1,NO
6610       ASPEC(I)=SPECIS(I)
6620   182 CONTINUE
6630C
6640   187 WRITE (NTWR,2490)
6650  2490 FORMAT (1X,'IF YOU WANT A LIST OF SPECIFIC REACTIONS,'/
6660      &         ' ENTER A TITLE (15A4) FOR EACH SEQUENCE,'/
6670      &         ' SEPARATING EACH ENTRY BY A CARRIAGE RETURN.'/
6680      &         ' INDICATE COMPLETION BY ENTERING A CR ONLY.')
6690       IF(NO.EQ.0) NO=999
6700       NUM=0
6710       K=0
6720  1905 READ (NTIN,2500) (STITLE(NUM+1,L),L=1,15)
6730  2500 FORMAT (1X,15A4)
6740       WRITE (IECHO,2500) (STITLE(NUM+1,L),L=1,15)
6750C
6760       IF(STITLE(NUM+1,1).EQ.IBLANK.AND.STITLE(NUM+1,2).EQ.IBLANK)
6770      & GO TO 1910
6780       NUM=NUM+1
6790       GO TO 1905
6800  1910 IF(NUM.EQ.0) GO TO 189
6810C
6820       WRITE (NTWR,2510)
6830  2510 FORMAT (1X,'ENTER THE NUMBER OF ENTRIES IN THE SEQUENCE,',/,
6840      &         ' AND THEN THE REACTION NUMBERS (I3),')
6850  1908 K=K+1
6860       WRITE (NTWR,2520) K
6870  2520 FORMAT (1X,'FOR THE SEQUENCE NO.: ',I2)
6880       READ (NTIN,2530) NLR(K), (LIST(K,M),M=1,NLR(K))
6890  2530 FORMAT (1X,I3,1X)
6900       WRITE (IECHO,2530) NLR(K), (LIST(K,M),M=1,NLR(K))
6910C
6920       IF(K.NE.NUM) GO TO 1908
6930C
6940C   NET RATES OF REACTION COMPUTED
6950C
6960   189 CALL RATES (C,N)
6970C
6980C
6990C
7000       GUESS=1.E-16
7010       IF (PPM.EQ.BLNK) GUESS=GUESS*60.
7020       DO 810 I=2,3
7030       YSTOR(I)=YMAX(I)
7040   810 CONTINUE
7050       T=TSTART
7060       IF(NFLG.NE.0) GO TO 1000
```

TABLE XIII

(continued)

```
7070C
7080C   INITIALIZE PARAMETERS
7090C
7100       IF(KOUT.EQ.0.OR.KOUT.EQ.2) GO TO 1000
7110       IF(ITITLE(1).NE.RIGO(2)) WRITE (IOUT,2640) (ITITLE(I),I=1,7),
7120      & (REAM(I),I=1,NM)
7130 2640 FORMAT (1H0,//,30X,7A4,//,23H INITIAL CONCENTRATION ,//
7140      &        (10X,10(4X,A4,4X)))
7150       IF(ITITLE(1).EQ.RIGO(2)) WRITE (IOUT,2680) (ITITLE(I),I=1,7)
7160 2680 FORMAT (1H0,//,30X,7A4,//)
7170       IF(ITITLE(1).NE.RIGO(2)) WRITE (IOUT,2650) (CC(I),I=1,NM)
7180 2650 FORMAT (/(8X,1P10E12.3))
7190       WRITE (IOUT,2660) TEMP,ERR
7200 2660 FORMAT (/,34H THE TEMPERATURE OF THE CELL WAS =,1PE9.2,
7210      &        26H AND THE ERROR TOLERANCE =,E9.2)
7220       WRITE (IOUT,2670) (R(I),I=1,NR)
7230 2670 FORMAT (/,29H THE RATE CONSTANTS USED WERE,/,(/,8X,1P10E12.3))
7240 1000 INDEX=1
7250       CALL YFIX (NS,TPRINT,C,NPRNT,INDEX)
7260C
7270C   USE THE GEAR ROUTINE
7280C
7290       IF(NFLG.NE.0) NFLG=0
7300       CALL DRIVES (NS,TSTART,TSTOP,C,GUESS,ERR,21,KFLAG)
7310       JFL=0
7320       IF(NFLG.NE.0) GO TO 990
7330C
7340C   WRITE END DATA AND 6-LINE BUFFER IN DATA FILE
7350C
7360       WRITE (I4051,2590) TOP,NS,NPNT,MTAB
7370 2590 FORMAT (1X,1PE12.3,3I5)
7380       DO 1078 M=1,6
7390       WRITE (I4051,2600) (PA(MM),MM=1,6)
7400 2600 FORMAT (1X,1P6E12.6)
7410 1078 CONTINUE
7420C
7430C   OUTPUT OF THE DILUTION FACTOR
7440C
7450       IF(KOUT.EQ.2) GO TO 1200
7460       IF(DILUT.NE.0.0) WRITE (IOUT,2710) DILUT
7470 2710 FORMAT (1H0,30H THE OVERALL DILUTION RATE WAS,1PE9.2)
7480C
7490C   TITLE CARD AND OPTIONS
7500C
7510 1200 IF(JPLOT.NE.0.AND.JFL.EQ.0) GO TO 1300
7520       WRITE (NTWR,2540)
7530 2540 FORMAT (1X,'ENTER AN OPTION CODE (A4): MORE'/
7540      &        1X,'                           CONT(INUE)'/
7550      &        1X,'                           HALT')
7560       READ (NTIN,2550) (ITITLE(I),I=1,7)
7570 2550 FORMAT (1X,7(A4,1X))
7580       WRITE (IECHO,2550) (ITITLE(I),I=1,7)
7590       NFL=0
7600C  RIGO(1) = "MORE"
```

TABLE XIII

(continued)

```
7610       IF(ITITLE(1).EQ.RIGO(1)) GO TO 800
7620C   RIGO(2) = "CONT"
7630       IF(ITITLE(1).EQ.RIGO(2)) GO TO 980
7640C   RIGO(4) = "HALT"
7650       IF(ITITLE(1).EQ.RIGO(4)) GO TO 9006
7660       GO TO 9006
7670C
7680C    CALL PLOT (MODK)
7690C
7700 1300 WRITE (NTWR,2560)
7710 2560 FORMAT (1X,'ENTER PLOT TITLE:')
7720       READ (NTIN,2570) (NIT(I),I=1,3)
7730 2570 FORMAT (1X,3A4)
7740       WRITE (IECHO,2570) (NIT(I),I=1,3)
7750       KALCMP=0
7760       JFL=1
7770       CALL PLOT (NIT,NT,NS,SPECIS,SAVTIM,SAVCON,KALCMP,JGRID)
7780       GO TO 1200
7790C
7800C    MORE DATA
7810C
7820  800 NS=NS-1
7830       NNY=NX+1
7840       N=NM
7850       NEW=0
7860       DO 805 I=1,NM
7870       C(I)=CC(I)
7880       REACT(I)=REAM(I)
7890  805 CONTINUE
7900       IF(KOUT.EQ.2) GO TO 806
7910       WRITE (NTWR,2690)
7920 2690 FORMAT (1H1)
7930  806 IND=0
7940       DO 993 I=1,10
7950       KCHNG(I)=0
7960  993 CONTINUE
7970       GO TO 1680
7980C
7990C    CONTINUATION OF DATA (CONT)
8000C
8010  980 IF(KOUT.EQ.2) GO TO 983
8020       WRITE (NTWR,2700)
8030 2700 FORMAT (1H1)
8040  983 WRITE (NTWR,2110)
8050       READ (NTIN,2120) TSTEP
8060       WRITE (IECHO,2120) TSTEP
8070       IF(TSTEP.EQ.0.) TSTEP=TPN
8080       TPRINT=TSTOP+TSTEP
8090       TSTART=TSTOP
8100       WRITE (NTWR,2130)
8110       READ (NTIN,2140) TMULT
8120       WRITE (IECHO,2140) TMULT
8130       WRITE (NTWR,2170)
8140       READ (NTIN,2180) TSTOP
8150       WRITE (IECHO,2180) TSTOP
```

TABLE XIII

(continued)

```
      DO 1599 I=1,NS
      C(I)=PA(I)
1599  REACT(I)=SPECIS(I)
      N=NS
      NI=NS
      NNY=NX
      NEW=0
      IND=0
      DO 992 I=1,10
      KCHNG(I)=0
 992  CONTINUE
      GO TO 1600
C
C   CHANGE K'S
C
 990  DO 991 I=1,NS
      C(I)=PA(I)
      REACT(I)=SPECIS(I)
 991  CONTINUE
      DO 811 I=2,3
      YMAX(I)=YSTOR(I)
 811  CONTINUE
      TSTART=CHANGE(IND)
      TPRINT=CHANGE(IND)+PC
       GO TO 189
9006  STOP
      END
```

language (object files), to eliminate the compilation process which otherwise needed each time we run CHEMK. The users should be aware that whenever she/he wanted to modify any of the subroutines, the modified version must be converted into object file otherwise computational activities would be terminated and the following error message will appear on the output.

<#32> Trace of call in reverse order

This conversion process from ASCII to object file is accomplished by running the compile file. The JCL for the compile file is presented below:

```
$$MONI

$$:IDENT:RCHMN001,EBRAHIM,XEQ COMPILE

$:FORTRAN NFORM,LNO,DECK,XREF,MAP

$:PRMFL:S*R,S,RCHM-LIB/DOTY/CHEMK/SOURCE/MAIN.S

$:PRMFL:C*,W,S,RCHM-LIB/DOTY/CHEMK/OBJECT/MAIN.C

$:END
```

Make sure that the name of the modified subroutine should be appear in the compile file. In this case subroutine MAIN has been used as an example. By running the compile file the source file (MAIN.S) which is in the ASCII format will be converted to Object file (MAIN.C).

CHEMK has the ability to retrieve previously stored reaction schemes of which there are nine in the library and two on my account. All chemical schemes can be accessed by the users. The available chemical mechanisms can be inspected in the MAIN subroutine and CHEMKRUN file. User to get a listing of these files should type

List RCHM-LIB/DOTY/CHEMK/DATA/file name

List RCHMN001/EBRAHIM/file name

where file name is the file of interest. These commands allow users to list the content of the file either from the library or from my account. These chemical mechanisms can be updated either directly by modifying the reaction schemes or indirectly by instructing the CHEMK via the command file (see command file below). For various editing capability of the Honeywell 66/40 see User guide manual.

How to run CHEMK

In order to run CHEMK the user should have four files in his account. These files are discussed below.

I. Command file

Create a file under any name in your account and then copy the content of the command file from my account. This process can be accomplished by typing

CPY RCHMN001/EBRAHIM/COMMAND;file name

where COMMAND is the prototype command file stored in my account. Once you transfered the command file into your account save it.

On the PSU computer (Honeywell 66/40), CHEMK must be run in a "batch" mode. That is, the program can not ask you direct questions, but can only read from, and write into files. CHEMK will type prompts to obtain the initial conditions for simulation. The listing of the inquiries are embedded in the MAIN subroutine (table XIII). The prompts to the inquiries are included in the command file. Example of a command file is presented in table (XIV).

In addition to the command file which controls the CHEMK activities, there are four other files you will need before you can run CHEMK. Three files (DAT 4051, NPROGD and DAT PLOT) need only to exist in your account. Their contents are unimportant. The DAT4051 and DATPLOT will recieve the result of CHEMK simulations and NPROGD acts as a buffer to keep a copy of the command file. This copy will be read for CHEMK execution from JCL commands (CHEMKRUN). The fifth file is commonly called JRUN file. A prototype of this file can be copied by typing the following command

CPY RCHMN001/EBRAHIM/CHEMKRUN; file name

where file name recieves the content of CHEMKRUN. The listing of this file is presented in table (XV). This file

TABLE XIV

CHEMK "COMMAND" FILE

```
91
9A
9FIL2L
90
9
915.
9
9
9360.
9303.
9
911
9
9M    =1.00E+06
9A    =1.00E+00
9NO   =5.00E-01
9PROP=1.00E+00
9H2O  =2.04E+04
9O2   =2.00E+05
9
9ALL
9
9HALT
```

TABLE XV

CHEMK "JRUN" FILE

```
$$MONI,J,T
$:IDENT:RCHMN001,EBRAHIM,CHEMISTRY--CHEMKRUN
$:OPTION:FORTRAN
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/MAIN.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/MANUAL.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/NOXX.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/PROH.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/CLOX.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/METH.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/HONO.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/FILE.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/SETUP.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/YFIX.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/ARATE.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/STIFF.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/DRIVES.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/COSET.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/DECOMP.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/SOLVE.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/CLEAN.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/RATES.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/DIFFUN.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/PEDERV.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/MATRX.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/PLOT.C
$:SELECT:RCHM-LIB/DOTY/CHEMK/OBJECT/LIBR.C
$:EXECUTE
$:LIMITS:10,70K,2,20K
$:PRMFL:07,R,S,RCHMN001/NPROGD
$:PRMFL:30,W,S,RCHMN001/DAT4051
$:PRMFL:31,W,S,RCHMN001/DATPLOT
$:FILE:32,NULL
$:PRMFL:21,R,S,RCHM-LIB/DOTY/CHEMK/DATA/PROPL
$:PRMFL:22,R,S,RCHM-LIB/DOTY/CHEMK/DATA/BUTXL
$:PRMFL:23,R,S,RCHM-LIB/DOTY/CHEMK/DATA/NOXWL
$:PRMFL:24,R,S,RCHM-LIB/DOTY/CHEMK/DATA/BUPRL
$:PRMFL:25,R,S,RCHM-LIB/DOTY/CHEMK/DATA/TOLHL
$:PRMFL:26,R,S,RCHM-LIB/DOTY/CHEMK/DATA/FIL1L
$:PRMFL:27,R,S,RCHMN001/FIL2L
$:PRMFL:28,R,S,RCHMN001/FIL3L
$:SYSOUT:06,ORG
$:ENDJOB
```

contains instruction to the computer, telling it how you want the program to run, where you want your output sent, etc. In this file you will have to change my user and I.D. to yours.

One pecularity of the Honeywell batch syastem is that all files used must be in BCD (Binary-Coded-decimal). Therefore, the user must convert the command file from ASCII to Binary. This conversion process can be accomplished by typing

CONV command file=command file:BCD

Now the file is in of a form that computer can read. If you wish to edit the command file at a later time, you must first convert it back to ASCII, by

CONV command file=command file:ASCII

Remember, the file must be in BCD to be read by the batch system. This is the most common error made in running CHEMK. Now you are ready to run CHEMK. Check once more to make sure you have three scratch files (DAT4051, DATPLOT and NPROGD), your command file and the batch system instruction file (JRUN). Now type JRN JRUN FILE and write down the snumb number to pick the CHEMK output from I/O window.

Retriving CHEMK output

If the data generated by the CHEMK is sent to the line printer, it can be picked up at the I/O window by asking for output for your snumb number.

If the data is sent to the line printer, the initial conditions (concentration, temperature and rate constants) are printed out as a document of the initial conditions for the data to follow. In addition to these output, each time we run CHEMK, the results of simulation will be written into file DAT4051 and DATPLOT. Through the proper interface (RS-238 GPIB) between Tektonix-4051 and Honeywell we can retrieve the CHEMK computed data. The steps which should be followed by users for retrieving data is presented below. First check the proper modem connection and turn the TEK 4051 on and type the following instructions sequentially.

a) call"cminit"

b) call"RSTRIN","","j","D"

c) Check that magnetic tape are marked properly (enough allocations for transfered data) and also magnetic tape should be in unsafe position. This information can be obtained by typing call"H" or if extended Basic Rom Pack is available for 4051 simply type "Directory". This command will give the type and the number of bytes allocation for the file.

d) call"TERMIN"

e) Push user definable key # 11 (PRINT CONTROL CHARACTER).

e) CONV DAT4051=**

NOTE: User at this part should not hit carriage return. If so go to step a and start over.

f) Push user definable key # 13 (FIND FILE)

g) Push user definable key # 3 (DATA RECIEVE)

After following properly these steps, the data will transfer from Honeywell to Tek 4051 and will be stored on the magnetic tape. The user can visually observe this transaction on the CRT. Once data transfer process completed then, hit break key twice and push user definable key # 1 (NORMAL CONTROL) and log off from Honeywell by typing "bye". The stored data on a magnetic tape have to be retrieved in a special format which could be read by the master program which do the plotting routines. This task is accomplished by running the Honeywell-Tek retrieving program. A listing of this retrieving program is presented in table (XVI). Through running this program, user will choose the species of interest and the program will search through data file to find the concentration-time coordinates of the desired species. The retrieved data then can be saved on a magnetic tape as a matrix for future data analysis.

TABLE XVI

HONEYWELL-TEK 4051 RETRIEVING
DATA PROGRAM

```
100 REM*******************************************************
110 REM*                                                     *
120 REM*    HONEYWELL-TEK 4051 RETRIEVING DATA PROGRAM       *
130 REM*                                                     *
140 REM*******************************************************
150 PRINT
160 DELETE A$,B$,D$,X
170 PRINT "HOW MANY DATA POINTS"
180 INPUT N
190 DIM A$(90),B$(2000),D$(3000),X(N)
200 B$=""
210 PRINT "FILE #"
220 INPUT H0
230 DIRECTORY
240 FIND H0
250 INPUT33:A$
260 GOSUB 1320
270 IF A$="" THEN 250
280 FOR I=1 TO 12
290 INPUT33:A$
300 GOSUB 1320
310 IF A$="" THEN 290
320 IF LEN(A$)=>72 THEN 350
330 A$=A$&" "
340 GO TO 320
350 B$=B$&A$
360 NEXT I
370 PRINT
380 FOR I=1 TO 12
390 FOR J=1 TO 6
400 A$=SEG(B$,72*(I-1)+12*(J-1)+4,5)
410 PRINT A$;"     ";
420 NEXT J
430 PRINT
440 NEXT I
450 REM*****Input the number and species of interest *****
460 PRINT " HOW MANY"
470 INPUT C1
480 DELETE D
490 DIM D(N,C1)
500 D=0
510 PRINT "  WHICH SPECIES"
520 INPUT X$
530 FOR K1=1 TO C1
540 A$=SEG(X$,(K1-1)*5+1,5)
550 P0=POS(B$,A$,1)
560 IF P0<>0 THEN 590
570 PRINT " NOT IN THE LIST"
580 GO TO 520
590 P0=INT(P0/12)
600 DIRECTORY
640 GOSUB 1320
650 IF A$="" THEN 630
660 FOR I=1 TO 12
670 INPUT33:A$
680 GOSUB 1320
690 IF A$="" THEN 670
700 NEXT I
```

(continued)

```
710 REM*************************************************
720 REM                                                 *
730 REM    ONCE HEADING READ,DATA WOULD BE READ.        *
740 REM*************************************************
750 FOR I=1 TO N
760 D$=""
770 FOR J=1 TO 12
780 INPUT33:A$
790 GOSUB 1320
800 IF A$="" THEN 780
810 D$=D$&A$
820 NEXT J
830 IF P0>0 THEN 860
840 A$=SEG(D$,2,12)
850 GO TO 900
860 IF P0=64 THEN 890
870 A$=SEG(D$,12*P0+5,12)
880 GO TO 900
890 A$=SEG(D$,12*P0+12,12)
900 X(I)=VAL(A$)
910 NEXT I
920 FOR J1=1 TO N
930 D(J1,K1)=X(J1)
940 NEXT J1
950 NEXT K1
960 PRINT D
970 DELETE A$,K$,C$,L$,E$,F$,G$,P$
980 DIM P$(200),C$(50),L$(50),E$(50),F$(50)
990 P$=""
1000 FOR I=1 TO 200
1010 P$=P$&" "
1020 NEXT I
1030 PRINT"RX NAME"
1040 INPUT A$
1050 PRINT "      DATA:  ";
1060 INPUT K$
1070 U$="
1080 PRINT U$;
1090 INPUT C$
1100 PRINT U$;
1110 INPUT L$
1120 PRINT U$;
1130 INPUT E$
1140 PRINT U$;
1150 INPUT F$
1160 M=C1
1170 FOR I=1 TO M
1180 PRINT "NAME OF SPECIES";I;":";
1190 INPUT U$
1200 GOSUB 1390
1210 P$=REP(U$,7*(I-1)+1,7)
1220 NEXT I
1230 PRINT" DATA TO BE RECORDED"
1240 INPUT S5
1250 DIRECTORY
1260 FIND S5
1270 U$=CHR(13)
1280 PRINT33:M,N,D,A$,U$,K$,U$,C$,U$,L$,U$,E$,U$,F$,U$,P$,U$
1290 CLOSE
1300 PRINT " DATA STORED"
1310 END
1320 Z$=CHR(127)
```

TABLE XVI

(continued)

```
1330 Z=POS(A$,Z$,1)
1340 IF Z=0 THEN 1370
1350 A$=REP("",Z,1)
1360 GO TO 1330
1370 RETURN
1380 U$=U$&" "
1390 GO TO (LEN(U$)>7)+(LEN(U$)=>7)+1 OF 1380,1420,1400
1400 U$=REP("",8,1)
1410 GO TO 1390
1420 RETURN
```